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AN INTRODUCTION

TO

CHEMICAL ANALYSIS

ROCKWOOD

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FOR STUDENTS OF MEDICINE, PHARMACY, AND DENTISTRY

BY

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PREFACE.

Although it may be desirable that elementary chemistry should be completed before the professional college is entered this is impractical in case of many American schools. The value of analytical chemistry in stimulating observation, power of discrimination, independence and self-reliance has long been recognized, as well as its services in affording an easy introduction to chemical work. It may, however, be carried on as a handicraft, without being of assistance in demonstrating the fundamentals of chemistry. The medical student not infrequently regards it as of no value except for the purpose of making analyses and for these he believes he will have little use. Though the importance of chemical analysis *per se* will probably always be slight, its points of contact with the other subjects in the medical curriculum are so numerous that, when rightly carried on, it not only stimulates interest in its own pursuit but gives a mastery over other branches which can be as easily attained in no other way.

The chemical incompatibility of medicinal substances is so intimately related to their chemical reactions that for their intelligent use a thorough acquaintance with the latter is a prerequisite. The same is true of the chemical antidotes for poisons. For this reason the reactions are quite fully given here. The properties and methods of manufacture of many substances employed for medical or dental purposes are also illustrated by the analytical reactions, which can therefore be used to impress them upon the mind of the student and thus make a connected chain of what is often learned as dismembered facts.

It is natural that chemical analysis for beginners should be differently conducted with professional students than with those who do not desire to apply it to any particular branch of knowledge. This book has been arranged for students of medicine, pharmacy and dentistry, much of whose territory is common. It assumes that some study has been devoted to general chemistry or that this is a contemporaneous course. It is designed to furnish a scientific basis for more technical courses but not to supplant these, and to give the familiarity with chemicals and manipulative methods, which is so necessary for real success in some lines of medical work.

There is no intention to make of the student an analytical chemist or mere mechanical manipulator. In many cases the work is abridged, as in the detection of poisons, where only the principal ones are considered or those which best illustrate the methods of such analysis. At the same time no attempt has been made so far to cut down the work that, with a mere smattering of knowledge, the student finishes, believing himself competent to meet all problems that he may encounter.

To accomplish the purposes outlined, series of questions have been inserted. The answers to these may be found partly in the experimental work previously done, and partly through reading in other departments of chemistry or of medicine. Others will suggest themselves to the instructor and it is only by insisting upon such outside study that the greatest value can be gained from such a course as this. If followed out they are a stimulus to individual application, they prevent mechanical working without thinking, and, by connecting chemical analysis with general chemistry, materia medica, physiology, toxicology, and other departments of medicine, they help to make clear the unity of the complete course.

But few equations have been given, and those usually only the more difficult ones. These benefit the student only when he can write them for himself and he should do this as far as possible in the time allowed. For a similar reason no tables are given for finding without labor the results of volumetric analyses. To represent the metric system as something more than a theory and to prepare for its future practical use all measurements are stated in metric denominations. Degrees of temperature are given by the centigrade thermometer.

While the length of the medical course often forbids any extended work in quantitative analysis some practical work in this is indispensable, partly in order to familiarize the student with the principles, partly because of its applications to other departments of medicine. Volumetric methods are admirably adapted for both these purposes and enough are given to illustrate the more common and to indicate how they may be extended. They include the preparation of the standard solutions, as well as the use of these, so that the student may, if necessary, be in condition to undertake the whole process in the practice of his profession and not be reduced to a state of helplessness if the emergency should arise. For the same reason, in a special table is included the preparation and testing of the qualitative reagents.

To make the course more interesting, by showing some of its applications, chapters are added on the testing of water, the detection of poisons, and analysis by means of the blow-pipe. While the latter is of subordinate importance for students of medicine and pharmacy it has, in this laboratory, proved itself of value is demonstrating to students of dentistry the physical and chemical properties of the metals and their alloys in a manner not possible by wet methods of testing. The length of the course can be

modified to fit the curriculum by omitting the less important parts or by varying the number of unknown substances to be analyzed under the separate divisions of the subject.

THE UNIVERSITY OF IOWA,
September, 1901.

PREFACE TO THE SECOND EDITION.

THE author has taken advantage of the demand for a second edition of this work to make correction of a small number of typographical errors which were found in the original. A few additions have been made, for the sake of greater completeness or where the suggestions of his colleagues have shown that it was advisable but the general plan of the book has not been changed. It is hoped that it will continue to commend itself to teachers.

THE UNIVERSITY OF IOWA,
September, 1904.

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TO THE STUDENT.

1. Perform no operation without a reason. Ask yourself in advance the object, and afterwards what has occurred; for example, in precipitating or washing,—what is removed? what remains?

2. Do your own work; use your own judgment, and let your neighbor do the same.

3. Avoid the use of an excess of materials or reagents. Add the reagent slowly, as much as is necessary and no more. Do not use concentrated acids unless they are specifically called for.

4. When a strongly acid solution, or one which gives an offensive odor is to be boiled, or when any acid solution is to be evaporated, do this under a hood that the gases may not remain in the room.

5. Except for cleaning, always use distilled water.

6. Always use pure chemicals for reagents, but never be sure that they are so without proving them.

7. Never put platinum wire, stirring rod or other object into a reagent bottle. Do not return to the bottle any reagent that has been removed.

8. In using the reagents never lay the stopper down. Hold it between the second and third fingers and replace it immediately in the bottle.

9. Do not throw into the sink concentrated acids, strong solutions of mercury or solid refuse like broken glass or filter paper. Put them in the waste jar.

10. Too great care cannot be exercised as to cleanliness. Have a cloth or towel and keep apparatus and desk in good order. Each student will be held responsible for the condition in which his desk is left.

INTRODUCTION.

The object of chemical analysis is the determination of the chemical composition of matter. This determination may be either of the kind of its components, or of their amounts. The methods used for the former belong to qualitative analysis; for the latter to quantitative.

In qualitative analysis the substance studied is not only examined alone but it is subjected to the action of certain forces, or of chemical compounds called reagents. These are designed to make more evident the physical properties of the substance or to produce characteristic compounds or changes. All such phenomena, called the reactions of the substance, can be used in its identification. Before entering upon the practical work of qualitative chemical analysis some explanation is demanded of the apparatus and reagents most in use, of the common processes, and of some of the terms employed.

In the majority of cases, although not always, the qualitative tests are made upon substances in solution. A solution is formed when a solid, liquid or gas is taken up by a liquid so that it loses its usual physical properties and can no longer be perceived. Solutions are regarded as of two kinds, physical and chemical.

Physical solutions are similar to those which result from mixing salt or sugar with water. There is no apparent chemical change in the substance dissolved, which is left unaltered when the solvent evaporates. In physical solutions of solids in liquids a rise in temperature, as a rule, increases not only the rapidity of solution, but also the amount of the solid capable of being dissolved. With solutions of gases in liquids the opposite is true and most dissolved

gases will be driven out of solution by an increased temperature.

Chemical solutions are such as the one formed when zinc is acted upon by an acid. The metal disappears but unites with the solvent so that when the latter evaporates an entirely different substance from the original one remains. In this case heating lessens the time of solution, but does not increase the amount of metal dissolved. In chemical solutions of gases, however, the gas is often expelled by heating, the compound being thus decomposed.

A concentrated solution is one in which the solvent contains a large amount of the dissolved substance; a dilute solution, one in which the amount dissolved is small. When the solvent contains as much of the dissolved matter as it can take up it is said to be saturated. A solution which has been saturated with a solid at a high temperature ordinarily deposits a part of the solid if the temperature falls. A few, as the temperature is decreased, will hold what has gone into solution, until the liquid is shaken or some solid matter is introduced, whereupon a large quantity of the dissolved material separates from the liquid. Solutions containing this excessive amount are said to be super-saturated. Where a solid remains floating in a liquid without dissolving it is said to be suspended, or in suspension.

Most solids which have been dissolved in a liquid and which afterwards separate through a change in temperature or a decrease in the volume of the solvent are crystalline in form. Such a method of preparation is called crystallization. A crystal is a solid which has a regular form bounded by plane surfaces, the angles between these being constant for the same species of crystal. Large crystals are produced only when they form slowly. It has been found that impure solids after having been dissolved

in water or other fluid and then allowed to crystallize leave most of their impurities in the liquid or "mother-liquor" so that this affords one of the best methods of purifying such substances.

For making solutions and for heating liquids the chemist commonly uses test-tubes, beakers or flasks of glass or dishes of porcelain. Test-tubes are made of thin glass and are designed to be heated in contact with the flame without breaking. The flame should, however, not be allowed to touch the tube above the liquid, since it easily becomes superheated there and breaks if moistened later.

FIG. 1.

Apparatus for solution. 1. Test-tubes in wooden support. 2. Beakers. 3. Iron stand with adjustable rings for supporting objects while they are heated. On one of the rings is a sand-bath. 4. Flasks.

The heat should not be applied to the bottom of the tube alone, as the steam bubbles thus produced might suddenly force the hot liquid from the tube, but all the parts of the liquid should be heated by moving and turning the tube in the flame. On account of this same danger the examina-

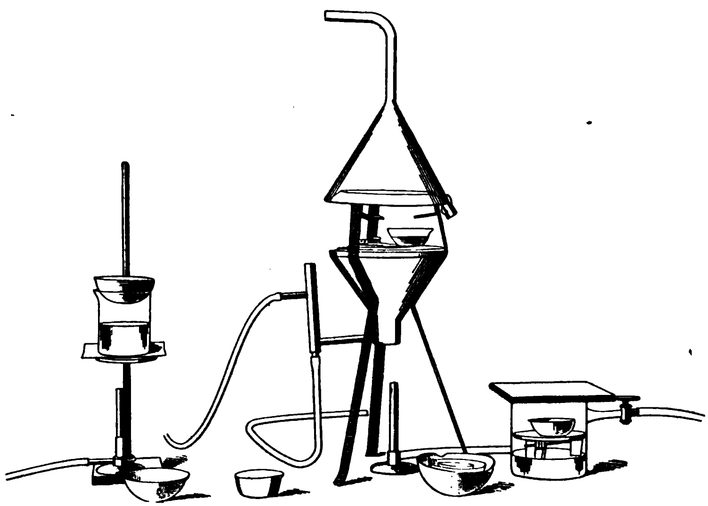
tions of the boiling substance should be made from the side and never from above and a test-tube while boiling should never be pointed toward another person. A tube half full can be brought to the boiling point while it is held in the fingers, although holders are sometimes used. If one is desired it can be made from a strip of paper which permits the rotation of the tube.

If long boiling is requisite a beaker is to be preferred to a test-tube. As these are somewhat thicker on the sides than at the bottom, they are not so well adapted to being heated in contact with the flame. They may be supported by an iron wire gauze or plate, which can be heated to a low redness without danger to the beaker if it contains a liquid. As with any other glass vessels they should not be heated above the liquid. Instead of the gauze or plate a sheet of asbestos is sometimes used, or a sand-bath,—that is a shallow iron dish with a thin layer of sand which distributes the heat evenly to the vessel. The two latter, although they are safe, waste more of the heat than does the gauze. Glass flasks can be used in the same way as the beakers. Evaporation is less from these than from beakers, which is often desirable. All glass vessels composed of the ordinary German glass are somewhat attacked by boiling water, and especially so by alkaline solutions. If great accuracy is desired those made of a resistant glass should be substituted for the former. Dishes of porcelain are but little affected by the ordinary reagents even at the boiling point, and the danger of their breaking is much less. A further advantage is that they may be heated with the naked flame. Liquids heated in them for a long time, however, suffer a considerable loss by evaporation.

Evaporation is the process by which a volatile substance may be separated from a less volatile solid or liquid, the

more volatile compound being allowed to escape. It may take place slowly at the ordinary temperature as, for example, when tinctures become more concentrated, through loss of alcohol, by standing in open bottles. It is hastened by the higher temperatures and is most frequently carried on by this means in chemical operations. Thus it is made use of in removing from solutions an excessive amount of

FIG. 2.

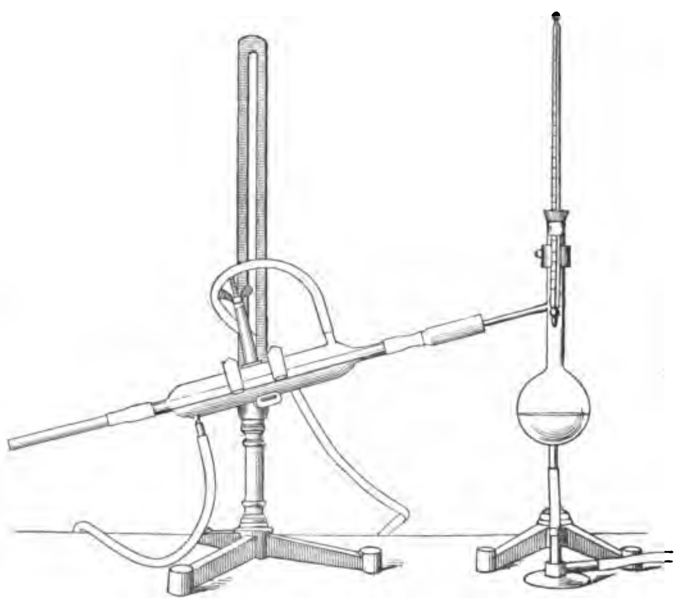


Apparatus for evaporation. 1. An extemporized steam-bath—a beaker of water on which a dish can be heated. 2. A copper steam-bath with tubes supplying water and allowing the excess to escape, thus maintaining a constant level. The funnel above excludes dust. 3. A sulphuric acid vacuum-desiccator connected with air pump. In front are evaporating dishes of porcelain, platinum and glass.

a volatile acid like hydrochloric, or even of one which is less readily converted to a gas, like sulphuric, in which case to effect its removal the liquid must be evaporated to dryness. When a liquid is to be evaporated a wide and shallow dish should be used as the vapors most easily pass

off from this. From a test-tube, on the other hand, evaporation is slow, the vapors condensing above to the liquid form, and flowing back into the tube. It is often advisable to conduct the process at some definite temperature, for instance not above 100°[1] in order to avoid burning or decomposition. This may be done by placing the liquid to be evaporated in a dish and setting this on a vessel in which water is boiling, known as a water-bath or steam-bath. For small operations a beaker will answer for the

FIG. 3.



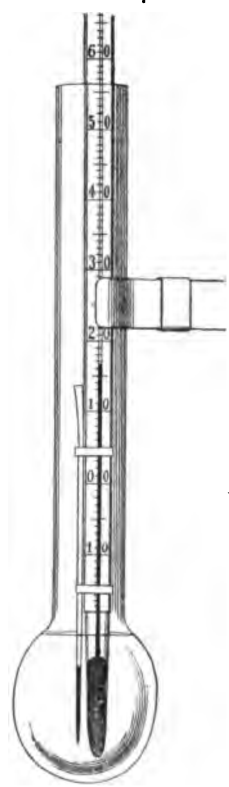
Apparatus for distillation. A flask connected with a Liebig's condenser and provided with a thermometer for showing the boiling point of the liquid which it contains.

lower vessel. All evaporations of injurious or offensive gases should be conducted in a hood or fume chamber,—

[1] In this work all temperatures are given in the centigrade scale, where the freezing point of water is at 0° and the boiling point 100°.

an enclosure connected with a ventilating shaft. Aqueous solutions can be evaporated at low temperatures by placing the dish over a vessel of some substance which has an affinity for moisture, like strong sulphuric acid, and placing over the whole an air-tight cover. This is called a desiccator. The process is much hastened by exhausting the air from the apparatus.

FIG. 4.



Apparatus for the determination of the melting point of a solid.

Distillation is similar to evaporation except that the expelled volatile substance does not escape but is collected by being again condensed to a liquid through cooling. This is commonly effected by passing the vapors into a tube which is surrounded by circulating cold water. If a thermometer is suspended with its bulb in the vapor during distillation it indicates the boiling-point of the liquid. This, with the melting-point, is of the greatest value in the identification of many compounds, especially the organic ones. The melting-point is determined after heating a short, small glass tube to redness in the middle, then drawing it out to a very small diameter. A piece of this, closed at the lower end, holds some of the powder beside a thermometer-bulb in a liquid, like water or sulphuric acid. By heating gradually until the powder melts, then reading the temperature, its melting-point is ascertained.

Precipitation is the process of changing dissolved sub-

stances into the insoluble state. It may be without chemical change, as when the dissolved matters of tinctures are precipitated by water, simply because they are insoluble in the latter. Or, on the other hand, the precipitate may be a new chemical compound which has been produced by the mutual decomposition of two dissolved substances, as when red mercuric iodid is formed by mixing a solution of potassium iodid with one of corrosive sublimate. Both varieties of precipitates are important in medicine and pharmacy but the latter will be the ones most frequently illustrated in qualitative analysis. They are usually heavier than the surrounding liquid and consequently settle to the bottom but some of the flocculent kinds float for a long time before sinking. Precipitation is valuable as a means of identifying an unknown metal since by this means characteristic compounds often appear; it is used to separate one substance from another by converting the one into an insoluble form; it is also of use in the preparation and purification of medicinal as well as other substances. Thus by the addition of a soluble carbonate to a calcium solution "precipitated chalk," a very pure form of calcium carbonate, is produced. When used for separation the filtrate must always be tested with more of the reagent in order to be certain that precipitation is complete.

A precipitate or other undissolved solid can be separated from a liquid in which it is suspended by filtration. To accomplish this the mixture is poured upon some porous material which allows the fluid to pass through but retains the solids. A porous paper is the most common filtering agent. It is supported in a glass funnel of such an angle that if a circular piece of the paper is folded in the center and then again in the center at right angles to the first fold it will when opened make a cone-shaped paper funnel which fits the glass exactly. To obtain the most rapid and

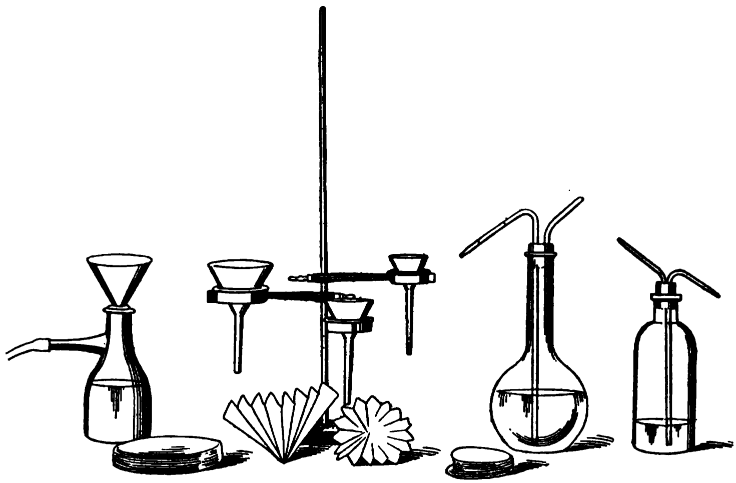
clean filtration it should be made to adhere to the sides of the funnel by moistening it with fluid of the same kind as that to be filtered and pressing it against the glass. It ought to be of such a size as not to reach quite to the rim of the funnel. The only ones of the common reagents which attack the cellulose of which the paper is composed are concentrated acids or strong solutions of sodium hydrate or potassium hydrate. The cheaper filter papers contain compounds of the metals, such as calcium and iron, and these may be dissolved by reagents which are being filtered, thereby rendering the latter impure. Where great accuracy is important the paper is, therefore, previous to being used, washed with hydrochloric or hydrofluoric acid to remove the impurities.

When it is desired to obtain the solution — called the filtrate — as quickly as possible without saving the precipitate, the plaited filter can be employed. This is made by folding double as before, and then into eight or sixteen folds, bending the paper each time in the same direction. Then each division is folded in the opposite way, without pressing at the tip, to avoid breaking, so that the filter looks like a closed fan. When it is opened the hollow cone has fluted sides, giving twice the surface of the plain filter. A plug of absorbent cotton loosely placed in the funnel is also convenient for obtaining the filtrate when the precipitate is to be discarded. Cotton consists, like the paper, of cellulose. Liquids which decompose cellulose should be filtered through asbestos or glass wool.

Many precipitates are so gelatinous that they clog the filter and the filtration proceeds very slowly. By passing the stem of the funnel through a rubber stopper into a vessel in which a partial vacuum can be created, the solution can be more rapidly drawn through the filter. The air may be exhausted from the vessel below by means of

a filter pump or aspirator attached to the water faucet of the laboratory. To avoid breaking the paper its tip must then be supported by inserting below it in the funnel a cone of platinum, muslin or some other strong material. It

FIG. 5.



Apparatus for filtration. 1. A funnel fitted to a filtering flask which is connected with a pump for the production of a vacuum and consequently an increase in the rapidity of the filtration. 2. A support holding funnels for filtration. 3. Washing bottles. In front are packages of filter paper with two plaited filters.

should be remembered that a hot solution generally filters more rapidly than a cold one.

After the precipitate has been collected on the filter it is usually necessary to further purify it by removing the liquid with which it is saturated and which contains soluble matters. This is done by washing, generally using for this purpose distilled water, the hot being ordinarily preferable to the cold. The water may be poured on from any vessel but is most conveniently applied from a washing-bottle. This is constructed of a bottle with a stopper perforated

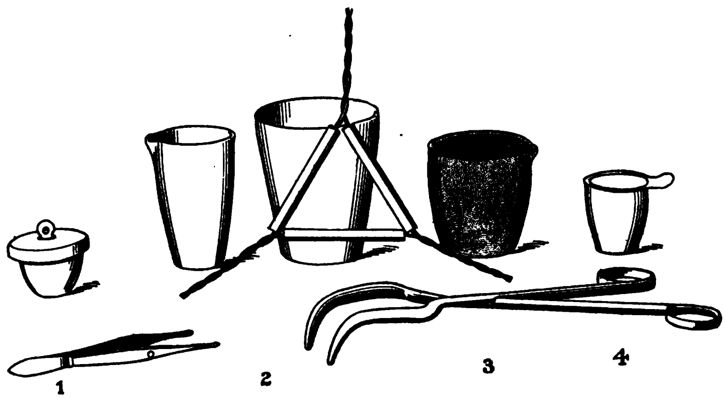
with two holes. Through one a long, bent tube passes to the bottom. It is contracted to a narrow opening at the outer end and serves for the exit of a jet which is forced out by blowing into the other opening through a short tube. By such a small stream the precipitate can be thoroughly mixed with the water and, if so desired, can be rinsed from the paper. For cold water any thick glass bottle of convenient size will serve, but if it is to be heated a thin-bottomed flask must be employed. Washing with hot water is more effectual than with cold. To ascertain whether the washing is complete a drop of the filtrate can be evaporated on a platinum foil and the amount of dissolved matter observed.

Sometimes when, in spite of the above methods, the filtration is very slow, it may be better to wash by decantation, — that is by letting the precipitate settle, pouring off the liquid without disturbing the solid and repeating as many times as is necessary. With heavy compounds like those of mercury this can be done very rapidly.

In order to produce certain chemical changes, or in the preparation of some substances, a higher degree of heat is required than that of boiling water. Even fusion, or melting, may be necessary. In many qualitative tests where small quantities of material are used the substance may be supported on a piece of charcoal, porcelain or platinum. The first necessitates the aid of the blowpipe; the second breaks too easily; the third is preferable because, while it is itself affected by few reagents and there is no danger of breaking, it permits a high heat to be attained. A pair of forceps or tongs will support it long enough in the flame to accomplish the fusion. With large quantities of material, or where the heating must be long continued a crucible can be advantageously substituted. These are most commonly made of platinum, porcelain, or clay.

Platinum is attacked by chlorin or by any mixtures, like aqua regia, which produce it. This is true not only during fusion but from solutions at low temperatures. It will also be affected by heating with fusible metals, since

FIG. 6.



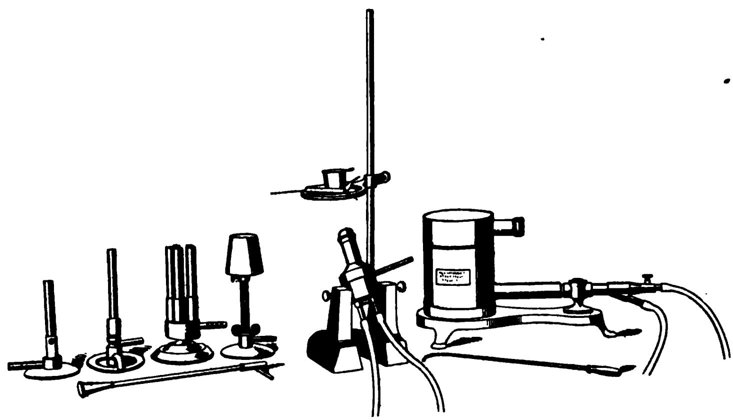
Apparatus for fusion. 1. Porcelain crucible. 2. Hessian or clay crucibles with a pipe stem triangle leaning against the middle one. On this the crucible can be supported while it is heated. 3. A graphite crucible. 4. A platinum crucible with cover. In front are forceps and crucible tongs.

these form alloys with it. Reducible compounds of such metals mixed with carbon should not be heated in platinum nor should the fusible sulphids or the caustic alkalies, all of which combine with it.

In the absence of illuminating gas the alcohol lamp will serve as a source of heat since it does not smoke cold objects held in the flame, while giving a great deal of heat. With gas, which is more convenient as well as cheaper than alcohol, the Bunsen burner is used. This consists essentially of a base, from which the gas is delivered by a small opening, and above this a tube with openings near the base through which is admitted the air which then mixes with the gas. This mixing brings about

the complete combustion of the carbon compounds of the gas, none being left to be deposited as soot, a high temperature being thereby produced. The openings below should be so regulated as to allow entrance to enough air to change the color of the flame from a yellow to a light blue. More than this lowers the temperature. With an excess of air, too, the flame often "strikes back" or burns within the tube at the bottom, changing in color first

FIG. 7.



I 2 3 4 5

Sources of heat. 1. Two forms of Bunsen burners. 2. A cluster of five Bunsen burners for greater heat. 3. A Bunsen burner with iron chimney to shut off drafts of air. 4. A blast lamp in position to heat the platinum crucible above. 5. A gas furnace for more intense heat with larger crucibles. In front are two forms of blowpipes.

to a yellow, afterwards to green. In this case the gas must be turned off, the size of the air vents reduced and the burner relighted.

For higher degrees of heat the blast-lamp will be advantageous. This is similar to the Bunsen burner, except that the air is forced in through one tube while the gas enters by another, the two mixing just before they are burned. A bellows or water-blast will furnish enough air

for this. For large crucibles there is less waste of heat if the crucible is surrounded by a fire-clay box or furnace and the flame from the blast-lamp is forced in below.

For the better examination of the products solid substances are occasionally heated or fused in a matrass. This is a glass tube closed at one end, thus resembling a small test-tube. It is made from a piece of straight glass tubing about 12 to 15 cm. in length and with a bore of about 4 mm. If this is heated in the middle until it is thoroughly softened, turning continually, it can be drawn apart while in the flame into two such matrasses. The long point can be removed by touching it while red hot with another piece of glass. It should be used for only one fusion.

FIG. 8.

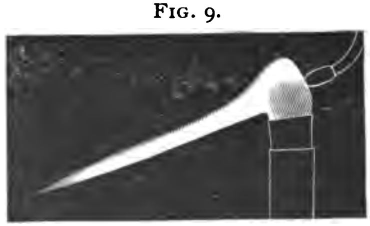
The flame of the Bunsen burner showing the four zones.

The flame of the Bunsen burner is not only a valuable agent as a heat-producer but also for the production of chemical changes. If the holes below are closed so that no air enters, the flame is luminous but smoky, depositing a coating of unburned carbon or soot upon a cold object held in it. The temperature is then not very high because of the incomplete combustion. As air is admitted the yellow color disappears and the flame becomes blue. There is an increase in temperature and objects heated are not smoked. An examination shows this flame to be composed of several parts. (*a*) At the base, within, is a blue cone varying in height with the amount of gas. This is a mixture of air and gas which is not being burned. If a splinter is thrust into it and held there it will burn at the

margin of the flame before the ignition of the inner end occurs. (*b*) This cone is outlined by a line of lighter blue. Here combustion is proceeding but not complete, there being present unburned carbon compounds of the gas. Under these conditions they will reduce oxygen compounds, that is remove the oxygen from them (reduction or deoxidation). This part of the flame is called the reducing or deoxidizing zone. A copper wire oxidized by holding it above the flame until it is black will lose its oxygen and its dark color after it is held a few seconds in it. (*c*) Outside the zone of reduction lies a wider zone, the hottest part of the flame, since in it combustion is complete. It i called the zone of fusion and should be used when heat alone is desired. (*d*) The outer margin of the flame is bluish white and rather indistinct. There the air is in excess and it is consequently able to oxidize, or give oxygen to, metals or other substances heated in it. It is called, therefore, the zone of oxidation or oxidizing zone.

In a similar manner the mouth blowpipe is made use of in effecting chemical changes. It is merely a bent tube of metal with a small opening through which air can be blown into a flame and the action of the latter can be thereby modified. The flame to be used is the yellow one made by closing the holes of the Bunsen burner or by slipping into it a smaller tube with a narrow opening above. This latter is preferable since less gas will be necessary and the flame can be better directed. To obtain an oxidizing action the yellow flame should be about 5 cm. high (2 inches) and, with the tip of the blowpipe just within the

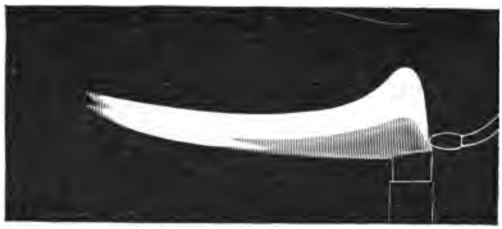
FIG. 9.



The oxidizing flame produced with the blowpipe (color, light blue).

flame, enough air should be used to make it blue, directing the blast through the greatest diameter of the flame. With the blowpipe also the blue flame should be employed when great heat is desired. For the reducing flame per-

FIG. 10.



The reducing flame produced by the blowpipe (color, yellow).

haps fifty per cent. more gas should be used; the blowpipe should be held outside the flame and only enough air be forced in to make the flame horizontal, not sufficient to change the yellow color to a blue. The reducing action is due here as in the Bunsen-burner flame to the incompletely oxidized hot carbon.

Since chemical action proceeds more readily between dissolved compounds than solids the reagents are in most cases used in solution. Unless for some particular reason, large amounts of these, and concentrated solutions, should be avoided. The dilute acids as a rule give better results than the concentrated. When the latter are required such directions will be given. In separating two or more metals an "excess" of the reagent must be used, but this does not imply an excessively large volume or weight. It means merely enough to do the work for which it is added. If this is precipitation enough must be used to completely remove the precipitable elements and the solution must afterwards be tested with more of the reagent to make sure that this has been done. If it is to acidify or make alka-

line a solution, the reagent should be slowly poured in and, after mixing, tests should be made to determine whether the liquid has the proper reaction.

The reaction of a solution or other substance is ascertained by its effect upon colored compounds, the one most commonly in use being litmus paper — that is paper colored blue, red or purple with a vegetable coloring matter, — litmus. If the liquid turns this red it is said to have an acid reaction; if it turns blue the reaction is alkaline. It is possible to make use of other colored substances besides this and a number will be so used in this course of study.

Soluble acids redden litmus paper, but an acid reaction in a liquid does not necessarily prove that a free acid is present, for other compounds can produce the same result. An acid is a compound of hydrogen with one or more negative (non-metallic) elements; and in the acids the hydrogen can be displaced by metals or similar substances and thus form a salt.

$$Zn + H_2SO_4 = H_2 + ZnSO_4.$$

Salts are therefore seen to be composed of a metal, or a similar substance, united with the negative part of an acid. They can also be formed by the action of an acid upon a base, which latter consists of a metal, or a group of elements of similar properties, combined with OH. In such cases water is produced at the same time.

$$NaOH + HCl = NaCl + H_2O, \text{ or}$$
$$2NH_4OH + H_2SO_4 = (NH_4)_2SO_4 + 2H_2O$$

In aqueous solutions such as are commonly used in analytical chemistry, we understand that the inorganic acids, bases and salts undergo a partial decomposition into their positive and negative components which are called

ions. These differ from the chemical elements in that they do not separate from the solution in such a way as to be visible. The degree of dissociation increases with the dilution and these ions are necessary for the reactions, in fact, without them there would probably be no chemical change in solution. Sulphuric acid, for instance, dissociates when diluted with water into hydrogen and SO_4. But if no water is present it is not dissociated and then the above reaction of the acid on zinc will not take place, as can be seen by putting zinc into concentrated acid. Just so with the other reactions of qualitative analysis, such as those for which the equations have been written,—in dilute solutions the compounds are mostly dissociated into ions. Thus in the above reaction between NaOH and HCl there would be in solution at first the ions $Na + OH + H + Cl$ and after the reaction $Na + Cl$ and water. This law of dissociation however does not apply to insoluble substances or precipitates. Accordingly the equations which follow have been written as if the elements were always united in compounds, but with the understanding that those in solution have, to a greater or less extent, undergone this form of decomposition.

The bases which are soluble in water change the color of red litmus paper to blue, or are alkaline in reaction; the insoluble bases do not affect the color.

Besides those changes where oxygen is removed from, or added to, a substance chemists sometimes speak of reduction or oxidation where other negative elements, like chlorin, are so removed or added, thereby decreasing or increasing the valence of the positive element. With some of these the reaction occurs when the dry substances are heated or triturated together. With others the change is effected in solution, either by the aid of heat or at the ordinary temperature. It may take place suddenly or may

require a long time for its completion. When the oxidizing agent is in the solid form the union may go on so rapidly as to cause a dangerous explosion. The production of either an oxidation or a reduction when medicinal substances are prescribed together is one form of incompatibility.

An incompatibility in a prescription is caused by such a selection or combination of the components that the usual action of these is modified or prevented and undesirable results follow. The incompatibility may be a pharmaceutical one, where there is no chemical change but a physical one, such as the separation of soluble matters from their solution. A therapeutical incompatibility occurs where drugs are prescribed together which are antagonistic in their physiological action upon the system. The third class, or chemical incompatibilities, is the only one with which this work will deal. In these the ingredients of the prescription act upon each other in such way as to produce a chemical change. It may not be a visible one, both or all resulting compounds remaining in solution; or, as is true in most instances, it may be perceptible. Some of the most common examples are those produced by the action of oxidizing agents which act both in dry mixtures, when explosions often occur, and in liquids. They are also caused by reducing agents, and in addition by those which without oxidation or reduction form insoluble substances or gases. In this manner the nature of the mixture may be entirely changed, perhaps being rendered inert on account of lessened absorption through its insolubility or, on the other hand, made more active or even poisonous through the formation of new compounds or by collecting the active principles in a precipitate which is taken with the last doses in the bottle. At times the incompatibility in a prescription is intentional, one of the ingredients being designed to

precipitate another, as in the combination of lime water and mercuric chlorid in the preparation of yellow wash. This, however, is infrequent. Many, although of course not all, of the chemical incompatibilities of medicinal compounds are illustrated by the reactions performed in the course of qualitative analysis. A thorough study should be made of these for the purpose of discovering such as are common or possible.

Where one or the other of the compounds entering into a reaction is a poison the results obtained in the following tests may often be used in the selection of an antidote. This may act by forming an insoluble compound with the poison and thereby preventing its absorption, by forming an inert compound through union, or by more complete decomposition of the poisonous substance. Only a knowledge of their chemical properties will give the physician a mastery over the subject of poisons.

PART I.

QUALITATIVE ANALYSIS.

CHAPTER I. METALS.

THE PREPARATION OF SOLUTIONS FOR ANALYSIS.

In dissolving solids for analysis no general rule can be given except that the weakest possible solvent should be employed, and of that only as much as is necessary. Heat is generally of great assistance in effecting solution. It is advisable first to learn the best solvent by testing small amounts of the solid, and, when this has been ascertained, to use as much as is desirable for the analysis. Solvents may be tried in a test-tube in the following order, always warming the liquid, and using separate portions of solid for each test.

1. Water.
2. Dilute hydrochloric acid.
3. Concentrated hydrochloric acid (2–4 cc.). Warm gently, afterwards dilute with water and boil.
4. Nitric acid, first dilute, then concentrated.
5. The residue from 3 in dilute, then concentrated nitric acid.
6. Aqua regia.

If concentrated acid is necessary it should be largely removed, by evaporating nearly to dryness under a hood, before proceeding to the analysis. If the solid dissolves in two separate solvents, the solutions may be mixed for the analysis unless this causes precipitation.

GROUP V.

The Alkaline Metals, Potassium, Sodium and Ammonium.

Almost all compounds of this group of metals are soluble in water, consequently they can rarely be identified by the formation of precipitates. Their hydrates, carbonates and also sulphids are alkaline in reaction.

Potassium, K.

Use a 5-per-cent. solution of KCl for the following reactions.

1. Dip a looped platinum wire into a potassium solution and hold it in the outer part of a Bunsen flame. The color of the flame above the substance becomes bluish-violet. Look at the flame through one or more thicknesses of blue glass (cobalt glass). The color is not destroyed by the glass but becomes a more distinct violet. No other metal will give these results, although many organic compounds give a luminous flame which appears of a similar color through the blue glass. The organic matter may be first destroyed by burning and then the residue tested for potassium.

2. Platinic chlorid, $PtCl_4$, precipitates potassium salts from neutral or alkaline solutions, if they are not too dilute, in yellow octahedral crystals of potassium platinum chlorid, K_2PtCl_6. The addition of alcohol renders the precipitation more complete.

Sodium, Na.

Use a 1-per-cent. solution of NaCl for the test.

3. Compounds of sodium give an intense yellow color to the flame when volatilized in it, as in the potassium tests, on a platinum wire. This color does not pass through a blue glass providing the latter is of sufficient thickness.

Ammonium, NH_4.

Use a 5-per-cent. solution of NH_4Cl for the reactions.

4. When ammonium salts, either solid or in solution, are heated with sodium hydrate, NaOH, they are decomposed, ammonia, NH_3, being liberated.

$$NH_4Cl + NaOH = NH_3 + NaCl + H_2O.$$

This is identified by its characteristic odor and also by its turning blue a moistened piece of red litmus paper suspended in the mouth of the test-tube in such a manner that it does not touch the inside of the tube. The hydrates of the alkaline earths and also of potassium will likewise set ammonia free from its compounds.

5. Platinic chlorid precipitates from neutral or acid solutions of ammonium salts, when they are sufficiently concentrated, yellow octahedral crystals of ammonium platinum chlorid, $PtCl_4(NH_4Cl)_2$. It is similar to the corresponding potassium compound.

6. All dry ammonium compounds are volatilized or decomposed when heated on platinum foil or a piece of porcelain.

7. A few drops of Nessler's reagent added to 10 cc. of a solution of an ammonia compound gives a brown precipitate, NHg_2I. The test is so sensitive that one part of ammonia can be detected in a million of water. With such dilute solutions there is no precipitate, but only a yellow to brown color produced.

Practical Exercise in the Analysis of Group V.

Mix in a test-tube 5 cc.[1] each of solutions of potassium, sodium and ammonium. Warm half of this with sodium

[1] It is advisable that the student should, at the beginning of his course, determine the volumes of his test-tubes and other vessels in metric measures and thereafter use only these measures in chemical work.

hydrate and observe that ammonia is set free, as from the single solution. Make the flame test with the other half, observing color both with and without blue glass. The sodium yellow is seen without the glass and the potassium violet with it, neither interfering with the other.

Questions for Further Study on Group V.

To be answered by the student.

How do you explain the destruction of the yellow light by the cobalt glass, while the violet passes through unchanged? What kind of chemical reagents turn red litmus blue? Why does the paper act more quickly if moist? Why should it not be allowed to touch the inner wall of the test-tube? Could the practical exercise above be used to determine the composition of an unknown mixture where K, Na and NH_4 might be present or absent? Can the dry sodium and potassium compounds be freed from ammonium compounds by heating to a high temperature? What compounds of the alkali metals would be incompatible with acids? What would be the best for neutralizing acids? What property of a chemical compound prevents its appearance as a precipitate? What compounds of ammonium can be identified by the odor? Which of the compounds of the alkali metals are suitable for internal use as antidotes in case of poisoning by the mineral acids?

GROUP IV.

The Metals of the Alkaline Earths, Magnesium, Calcium, Strontium and Barium.

Their oxids are soluble in water (Mg only slightly so), and the solution has an alkaline reaction. The phosphates and carbonates are insoluble in water but soluble in acids, except sulphuric, the carbonate yielding CO_2 and neutral-

izing the acid. Their arsenates and arsenites do not dissolve in water. None of them are precipitated by hydrogen sulphid or ammonium sulphid.

Take for each test 3–4 cc. of the solution of their salts.

Magnesium, Mg.

Use a 5-per-cent. solution of $MgCl_2$ for the reactions.

8. From solutions of magnesium salts ammonium carbonate precipitates, on standing or warming, magnesium carbonate, variable in composition but usually $MgCO_3, 3H_2O$ or $(NH_4)_2Mg(CO_3)_2, 4H_2O$,

$$MgCl_2 + (NH_4)_2CO_3 + 3H_2O = MgCO_3, 3H_2O + 2NH_4Cl.$$

$$MgCl_2 + 2(NH_4)_2CO_3 + 4H_2O = (NH_4)_2Mg(CO_3)_2, 4H_2O + 2NH_4Cl.$$

This precipitate is soluble in solutions of ammonium salts. It will therefore disappear on adding ammonium chlorid and heating. If the ammonium chlorid is added to the magnesium solution before the ammonium carbonate there will be no precipitation of magnesium carbonate.

9. Sodium phosphate, with ammonium chlorid and ammonium hydrate, precipitates magnesium solutions as white, crystalline ammonium magnesium phosphate, NH_4MgPO_4.

$$MgCl_2 + Na_2HPO_4 + NH_4Cl + NH_4OH = NH_4MgPO_4 + NH_4Cl + 2NaCl + H_2O.$$

Under the microscope the crystals are seen to have a stellate or fern-leaf form, especially if quickly precipitated. When formed very slowly they are prismatic. All precipitates of magnesium are soluble in acids.

10. Sodium carbonate, with neutral solutions of magnesium salts, gives a white precipitate of basic magnesium

carbonate, variable in composition but essentially $Mg(OH)_2$-$4MgCO_3$. It is a very light, white solid, soluble in ammonium salts and becoming heavier by heating in the solution.

11. Ammonium hydrate, sodium hydrate or potassium hydrate precipitates magnesium as magnesium hydrate, $Mg(OH)_2$, which action is prevented, or the precipitate is re-dissolved, by ammonium salts.

Calcium, Ca.

Use for reactions a 5-per-cent. solution of $CaCl_2$.

12. Calcium salts when held in the blue Bunsen flame give it a yellowish red color. This is destroyed by the blue glass, through a thin piece of which it appears grayish green. The flame test is most marked with the chlorid or, when other salts are tested, after moistening with hydrochloric acid.

13. Ammonium carbonate or other soluble carbonates precipitate calcium as calcium carbonate, $CaCO_3$, white and amorphous, and practically insoluble in ammonium salts. If, after settling, the solution is separated from the precipitate, the latter will dissolve with effervescence when an acid is poured on it.

14. Ammonium oxalate produces a fine, white precipitate of calcium oxalate, CaC_2O_4 from neutral or alkaline calcium solutions.

$$CaCl_2 + (NH_4)_2C_2O_4 = CaC_2O_4 + 2NH_4Cl.$$

It is soluble in strong acids.

15. Sulphuric acid, or soluble sulphates precipitate from a concentrated solution, fine, white, calcium sulphate, $CaSO_4$, which is soluble in a large amount of water. It is, in consequence, not precipitated from dilute solutions. Calcium salts are not precipitated by a solution of calcium sulphate.

16. Sodium phosphate or other soluble phosphates throw down from calcium solutions a white, flocculent acid calcium phosphate, $CaHPO_4$.

17. Potassium dichromate does not precipitate calcium from its solutions.

Strontium, Sr.

A 5-per-cent. solution of $SrCl_2$ may be used for the reactions.

18. Strontium salts give a deep crimson color to the blue flame, best after the addition of hydrochloric acid. This is seen through a thin blue glass but not through a thick one.

19. Ammonium carbonate, or other soluble carbonates, give a white, flocculent precipitate of $SrCO_3$, similar in properties to $CaCO_3$.

20. Ammonium oxalate precipitates strontium oxalate, SrC_2O_4, if the solution is not very dilute. It is a fine white powder.

21. Sulphuric acid precipitates strontium as the sulphate, $SrSO_4$, the same result being obtained by the use of calcium sulphate and other soluble sulphates. The strontium sulphate is somewhat soluble in water, consequently it is not completely precipitated and appears rather slowly in dilute solutions. It is less soluble in alcohol.

22. Sodium phosphate produces a white, flocculent precipitate of $SrHPO_4$, acid strontium phosphate.

23. Potassium dichromate does not precipitate strontium from its neutral or acid solutions.

Barium, Ba.

All soluble barium compounds act as poisons.

Use for the reactions a 5-per-cent. solution of $BaCl_2$.

24. Barium chlorid and most other barium salts to which hydrochloric acid has been added produce a yellowish-

green color when held in the oxidizing flame of a Bunsen burner.

25. Ammonium carbonate or other soluble carbonates precipitate barium from its solution as $BaCO_3$, similar in its properties to the carbonates of calcium and strontium.

26. Ammonium oxalate forms barium oxalate, BaC_2O_4, a fine, white, heavy precipitate.

27. Sulphuric acid or any soluble sulphate precipitates immediately the barium from its solution as a heavy, very fine, white solid, — barium sulphate, $BaSO_4$.

28. Sodium phosphate forms barium phosphate, $BaHPO_4$, a compound similar in composition, formation and properties to the corresponding salts of calcium and strontium.

29. Potassium dichromate, $K_2Cr_2O_7$, or chromate, K_2CrO_4, precipitate bright yellow barium chromate, $BaCrO_4$, insoluble in acetic acid.

Directions for the Analysis of Groups IV and V.

If the solution which contains the bases of groups IV and V is not already alkaline make it so by adding a little ammonium hydrate, then about 5 cc. of ammonium chlorid and, finally, ammonium carbonate as long as a precipitate is formed. Warm nearly to the boiling-point and filter. Wash the precipitate, discarding the wash-water.

The precipitate contains the carbonates of barium, strontium and calcium. The filtrate contains magnesium, potassium, and sodium.

Dissolve the precipitate on the paper by pouring over it 5–10 cc. of hot acetic acid, using the same acid repeatedly if the first application is insufficient. To the resulting solution add potassium dichromate which precipitates the barium as yellow barium chromate. Filter and, after diluting the filtrate with water to about 25 cc., add dilute

sulphuric acid to precipitate the strontium. The precipitate of strontium sulphate is a very fine, white solid. Let it settle five minutes. Filter, wash, moisten the precipitate on the filter with a few drops of hydrochloric acid and confirm the presence of strontium by the deep crimson color imparted to the flame of a Bunsen burner when the substance is held in it on a platinum wire. It is also reddish through the cobalt glass. Make the filtrate from the strontium alkaline with ammonium hydrate, then add ammonium oxalate. Calcium is precipitated as fine, white calcium oxalate. It may be confirmed by the reddish-yellow color of its flame, testing in the same manner as for strontium. It appears a dirty green through a thin blue glass.

The solution containing magnesium, potassium and sodium should be tested first for the sodium and potassium by the color imparted to a Bunsen-burner flame—yellow from sodium, and violet when potassium is present and the flame is viewed through a sufficiently thick blue glass. The test is more delicate, with small amounts of these metals, if the liquid is first concentrated to a few cubic centimeters by boiling.

To detect magnesium add to the solution which has been tested for sodium and potassium a little sodium phosphate. Shake vigorously and let it stand without warming. Magnesium ammonium phosphate is precipitated—small, white, snowflake-shaped crystals, when seen with the microscope. An excess of ammonium hydrate favors the precipitation. The presence of ammonium in the original substance can be determined only by applying the test to this directly. This is done by adding 5 cc. of sodium hydrate, or enough to give an alkaline reaction, and boiling. The ammonia gas which is evolved can be identified by its characteristic odor or by its turning red litmus paper blue.

TABLE I.

OUTLINE OF SEPARATIONS OF METALS OF GROUPS IV AND V.

Heat a small portion of the original substance with sodium hydrate. An evolution of ammonia gas indicates ammonium.

Make the remainder of the solution which contains groups IV and V alkaline with ammonium hydrate and add ammonium chlorid and ammonium carbonate, filter and wash.

<table>
<tr><td colspan="3">Precipitate contains $BaCO_3$, $SrCO_3$, $CaCO_3$. Dissolve in dilute acetic acid and add potassium dichromate. Filter.</td><td rowspan="3">Filtrate contains Mg, K and Na. Test color of flame. Yellow indicates Na. Violet through the blue glass indicates K. Add sodium phosphate. A white, crystalline precipitate indicates Mg.</td></tr>
<tr><td rowspan="2">A yellow precipitate is $BaCrO_4$.</td><td colspan="2">Solution contains Sr and Ca. Add dilute H_2SO_4.</td></tr>
<tr><td>A fine white precipitate is $SrSO_4$. Confirm by crimson flame.</td><td>Solution contains Ca. Make alkaline with ammonium hydrate and add ammonium oxalate. A fine white precipitate is CaC_2O_4. Confirm by reddish yellow flame.</td></tr>
</table>

Explanations of the Operations Used in the Separation of the Metals of Groups IV and V.

The ammonium chlorid must be used here to prevent the precipitation of magnesium with the others of the alkaline earth metals (8). Ammonium hydrate is necessary to neutralize any acid that may be present as this would decompose the ammonium carbonate and prevent the precipitation of any of the metals. The carbonates of barium, strontium and calcium which are formed in cold solutions are not completely precipitated if carbon dioxid is present because of the formation of soluble acid carbonates, but these are converted by heating into insoluble carbonates.

The carbonates are converted to acetates by the application of acetic acid, and the latter are soluble. The majority of precipitates are not soluble with sufficient ease to

allow this method of solution but must be removed from the filter and mixed, or often heated, with the solvent. The effervescence is caused by the evolution of CO_2 which is always set free by the action of an acid on a carbonate. If no water were added to the solution of strontium and calcium before the former was precipitated as a sulphate some or most of the calcium would also be thrown down (15). Strontium is slowly precipitated on account of the solubility of its sulphate (21), therefore, it is necessary to allow sufficient time for this to be accomplished.

If the strontium sulphate were not washed some of the calcium solution would remain, if this metal were present in the mixture, and the color of the flame would be modified. The acid makes it more distinct.

Ammonium oxalate does not precipitate bases of this group from acid solutions, such as this one is after the use of sulphuric acid, consequently the latter must be neutralized in order to detect the calcium.

The flame test for the alkalies should not be made until the removal of the above metals from the mixture because of the effect they would give if they were present. The sodium would not be concealed but the potassium might be difficult of identification (18).

The test for sodium must be applied before that for magnesium because the precipitation of magnesium requires a sodium salt and the sodium from this remains in solution and passes into the filtrate from the magnesium. With solid sodium compounds or very strong solutions some of the light may pass through the cobalt glass if this is not sufficiently thick but it is then blue and not violet, as can be seen by comparing it with a known potassium solution.

The sodium phosphate precipitates the magnesium very completely but if there is not much magnesium present a long time of standing may be necessary.

The original substance can be tested for ammonium by adding sodium hydrate to it directly without dissolving as the ammonia will be readily set free. If only a minute amount is present it can be detected by hanging the moist red litmus paper, in such a manner that it shall not touch the tube, from a cork which closes the test-tube and allowing it to stand for twenty-four hours at the ordinary temperature. It is necessary to use the original substance to test for ammonia and not the filtrate from barium, strontium and calcium carbonates where we might naturally look for it, since before getting this filtrate a number of ammonium compounds have been added to the solution.

Practical Exercises in the Separation of the Metals of Groups IV and V.

Mix in a large test-tube 3–4 cc. of the solution of each metal and analyze the mixture of the seven according to Table I.

In the same manner make analyses of unknown mixtures of the metals of these groups, which can be obtained from the instructors, and report results in writing.

Questions for Further Study on Group IV.

Why are the bases of group IV called metals of the alkaline earths? When their oxids dissolve in water is there any chemical change? What is such a solution of calcium called? For what is it used? What property of these compounds is made use of to separate the bases of this group from those of group V? What is meant by effervescence? Why might it be expected that the flame of calcium compounds would be more plain by the addition of hydrochloric acid? What would be the effect of adding alcohol to a mixture of sulphuric acid with a dilute solution of strontium? Why does not calcium sulphate precipitate

concentrated solutions of calcium salts when this can be done by the use of other soluble sulphates? Why will ammonium oxalate not precipitate calcium from a strongly acid solution? In the analysis of group IV what would be indicated if, instead of a crystalline precipitate where we should expect magnesium, a white amorphous precipitate should appear? Are there any other alkaline gases except ammonia? Which compounds of the metals of group IV can be employed for the neutralization of acids? Are any ever used medicinally for this purpose? Can an acid be neutralized by a substance which is itself neutral in reaction? What use is made of calcium carbonate in medicine? By what other name is magnesium carbonate known, and for what properties is it valuable in medicine? What is the difference in composition between the soluble acid carbonate of calcium and the insoluble carbonate of the same metal? Where does the former occur naturally?

GROUP III.

Aluminum, Chromium, Zinc, Manganese, Cobalt, Nickel and Iron.

Not only the carbonates and phosphates of this group are insoluble in water but also the oxids, hydrates and sulphids, except the sulphids and carbonates of aluminum and chromium. The members of the group are therefore precipitated in neutral solutions by soluble hydrates, carbonates, phosphates, and sulphids. Hydrogen sulphid does not precipitate metals of this group from acid solutions.

Aluminum (Aluminium), Al.

Aluminum dissolves in hydrochloric acid and caustic alkalies, but only slowly in most other acids.

Use for the reactions a 5-per-cent. solution of $Al_2(SO_4)_3$ or $KAl(SO_4)_2$.

30. Ammonium sulphid produces in aluminum solutions a very light, gelatinous, white precipitate of aluminum hydrate, $Al(OH)_3$.

$$Al_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O = 2Al(OH)_3 + 3(NH_4)_2SO_4 + 3H_2S.$$

It is readily soluble in acids.

31. Ammonium hydrate precipitates from aluminum solutions aluminum hydrate as in the last reaction. It is slightly soluble in large excess of the reagent but is precipitated completely by heating.

32. Alkaline carbonates with alum solutions form the same compound, CO_2 escaping.

$$2KAl(SO_4)_2 + 6NaHCO_3 = 2Al(OH)_3 + K_2SO_4 + 3Na_2SO_4 + 6CO_2.$$

33. Sodium hydrate or potassium hydrate gives with aluminum salts a precipitate of aluminum hydrate as above. It dissolves immediately in an excess of the reagent with the formation of an aluminate, as $NaAlO_2$. From these solutions the metal cannot be precipitated by the above-mentioned reagents but can be by the addition of ammonium chlorid, best with the aid of heat. Acidifying the solution of an aluminate converts the compound again into an aluminum salt of the acid used, *e. g.*, with sulphuric acid aluminum sulphate is formed.

34. Barium carbonate, when shaken with an aluminum solution and allowed to stand in the cold, precipitates the whole of the aluminum as a basic salt as is shown by the absence of aluminum reactions in the filtrate.

Chromium, Cr.

Chromium may be met with in two classes of compounds: the salts, where the metal occupies the positive part of the compound like $CrCl_3$ or $Cr_2(SO_4)_3$; and the chromates, or

chromic acid derivatives, where it is found in the negative part, such as $PbCrO_4$ or $K_2Cr_2O_7$. With these two classes most reagents give different results. The former will be considered in this place; the latter, under chromic acid.

The chromic salts have a green or violet color, this being true of their solutions also.

Use for the reactions of the chromic salts a 5-per-cent. solution of $KCr(SO_4)_2$.

35. Ammonium sulphid with solutions of chromium salts gives a precipitate of chromium hydrate, $Cr(OH)_3$, a grayish-green or bluish-green, voluminous gelatinous compound. It is soluble in acids. Hydrogen sulphid is set free in the precipitation as it is by the action of ammonium sulphid on aluminum salts.

36. Ammonium hydrate precipitates from chromium salts chromium hydrate. It is slightly soluble in excess of the reagent imparting a pink color to the liquid, but is precipitated from this solution by boiling.

37. Sodium hydrate or potassium hydrate with solutions of chromium salts causes a precipitation of the same compound, chromium hydrate. In excess of these reagents the precipitate is easily soluble to a green liquid. On boiling, the liquid becomes colorless, the chromium being again precipitated as the hydrate.

38. Dry compounds of chromium if mixed with dry potassium or sodium nitrate and sodium carbonate and then fused on the platinum foil are thereby converted to yellow potassium or sodium chromates. These are soluble in water, forming a bright yellow liquid and giving the reactions of chromic acid (p. 107). For this test any of the precipitates may be employed after filtering from the solution and drying on the foil.

$$Cr_2(OH)_6 + 3NaNO_3 + 2Na_2CO_3 = 2Na_2CrO_4 + 3H_2O + 2CO_2 + 3NaNO_2.$$

39. Barium carbonate precipitates basic chromium salts in the same manner as those of aluminum.

Zinc, Zn.

Zinc is readily soluble in hydrochloric, nitric and sulphuric acids. Its salts are colorless.

For the reactions a 2-per-cent. solution of $ZnSO_4$ may be used.

40. Ammonium sulphid precipitates zinc from its neutral or alkaline solutions as the sulphid, ZnS. It is a white, flocculent solid, insoluble in excess of the reagent or in alkalies but soluble in most mineral acids.

41. Ammonium hydrate with zinc solutions precipitates zinc hydrate, $Zn(OH)_2$, a white gelatinous compound readily soluble in excess of ammonia. On boiling, the zinc hydrate precipitates again in whole or in part unless ammonium salts are present, which will prevent the separation.

42. Sodium hydrate or potassium hydrate produces in zinc solutions a white gelatinous precipitate of zinc hydrate. It dissolves in excess of the precipitant. It does not precipitate from this solution upon boiling if a large excess of the alkali is present.

43. Potassium ferrocyanid precipitates zinc ferrocyanid, $Zn_2Fe(CN)_6$, a white compound, insoluble in cold dilute hydrochloric acid but somewhat soluble in an excess of the reagent.

44. Barium carbonate does not precipitate zinc salts.

Manganese, Mn.

Metallic manganese dissolves easily in acids with the formation of manganous salts.

Use for the reactions a 2-per-cent. solution of $MnSO_4$.

45. Ammonium sulphid precipitates manganese from its solutions as the sulphid, MnS, a flesh-colored compound

which upon standing exposed to the air becomes dark brown. This precipitate is insoluble in excess of the reagent but dissolves readily in acids.

46. Sodium hydrate or potassium hydrate produces a precipitate of manganous hydrate, $Mn(OH)_2$, which is at first nearly white but when shaken in the tube with air, or allowed to stand exposed to it, becomes quickly dark brown from the absorption of oxygen and the formation of manganic hydrate, $Mn(OH)_3$. The precipitate is insoluble in excess of sodium hydrate but dissolves in acids.

47. Ammonium hydrate also gives a precipitate of manganous hydrate, insoluble in excess, but with this reagent the precipitation is prevented by the presence of ammonium chlorid.

48. If as much Pb_3O_4 (red lead) as can be held on the point of a pen-knife is added to a manganous solution and if the mixture is then strongly acidified with nitric acid, boiled and allowed to settle, the liquid above has a red color. The presence of hydrochloric acid or chlorin compounds interferes with, or prevents, the reaction.

$$2MnSO_4 + 5Pb_3O_4 + 26HNO_3 = 2HMnO_4 + 13Pb(NO_3)_2 + 2PbSO_4 + 12H_2O.$$

49. Solid compounds of manganese when mixed with several times their weight of dry sodium carbonate and potassium nitrate and fused on the platinum foil become converted to green sodium manganate, Na_2MnO_4, the color of which is best seen while it is melted.

$$Mn(OH)_2 + Na_2CO_3 + 2KNO_3 = Na_2MnO_4 + 2KNO_2 + H_2O + CO_2.$$

If too much of the manganese compound is used the mass may be black. In the cold it dissolves in water to a green solution. This is decomposed by boiling the liquid,

the manganese being precipitated as an oxid. The green solution is gradually changed to a pink through exposure to the air, the manganate being converted to a permanganate, $NaMnO_4$.

50. Manganous compounds are not precipitated from their solutions by barium carbonate.

Iron, Fe.

The metal is soluble in hydrochloric, sulphuric and nitric acids. There are two series of salts, the ferrous and the ferric. The former are, for the most part, colorless or greenish and unite with oxygen when brought in contact with oxidizing agents, or even when exposed to the air, especially in the presence of water. They are thus converted into ferric salts which are usually yellowish to reddish-brown.

Ferrous Compounds (Fe'').

For the reactions use a 2-per-cent. solution of $FeSO_4$.

51. Ammonium sulphid precipitates the iron completely from neutral or alkaline solutions as black ferrous sulphid, FeS. This dissolves in dilute acids and oxidizes in the air to brown ferric hydrate.

52. Ammonium hydrate produces ferrous hydrate, $Fe(OH)_2$. If the ferrous solution is pure and oxygen is excluded from that and the reagent the color at first is nearly white. Without these special precautions, however, it is a grayish-green, which soon changes by oxidation to a darker green and finally is converted to reddish-brown ferric hydrate, $Fe(OH)_3$. This precipitation is prevented by the presence of non-volatile organic acids or their salts and by ammonium salts; also by other organic compounds like sugar and glycerin.

53. Sodium hydrate or potassium hydrate precipitates ferrous hydrate, having the properties given above.

54. Potassium ferrocyanid, $K_4Fe(CN)_6$, with solutions of ferrous salts which are free from ferric compounds gives a bluish-white precipitate of potassium ferrous ferrocyanid, $K_2Fe_2(CN)_6$. This becomes deep blue by the action of the oxygen of the air or by oxidizing agents. Hydrates of the alkalies destroy the blue color.

55. Potassium ferricyanid, $K_3Fe(CN)_6$, with ferrous solutions produces a deep blue precipitate of ferrous ferricyanid, $Fe_3''Fe_2'''(CN)_{12}$. Hydrates of the alkalies decompose this. With very dilute solutions of iron the last two reagents produce only a greenish color.

56. Potassium sulphocyanate, KSCN, imparts no color to ferrous solutions if they do not contain ferric compounds.

57. Sodium carbonate, or ammonium carbonate, precipitates ferrous solutions as white ferrous carbonate, $FeCO_3$, which, when moist, rapidly oxidizes in air, giving up its CO_2, ferric hydrate, $Fe(OH)_3$, being formed.

58. Barium carbonate does not precipitate ferrous salts in the cold with the exception of ferrous sulphate.

59. Tannic or gallic acids produce no color with ferrous solutions if they are free from ferric salts.

Ferric Compounds (Fe''').

For the reactions use a 2-per-cent. solution of $FeCl_3$.

60. Ammonium sulphid precipitates ferric salts as ferrous sulphid, FeS, sulphur being set free.

$$FeCl_3 + (NH_4)_2S = FeS + NH_4Cl + S.$$

61. Ammonium hydrate or other soluble hydrates precipitate ferric solutions as ferric hydrate, $Fe(OH)_3$, a reddish-brown, gelatinous substance. It cannot be thus formed in solutions containing a large amount of non-volatile organic acids, sugar or glycerin. It dissolves readily in acids, but is insoluble in excess of the precipitant and in solutions of ammonium salts.

62. Potassium ferrocyanid with ferric solutions gives a dark blue precipitate of ferric ferrocyanid, $Fe_4'''Fe_3''(CN)_{18}$ —"Prussian blue." This is insoluble in hydrochloric acid but is decomposed by the alkaline hydrates with the separation of ferric hydrate, similarly to the decomposition of ferrous ferrocyanid.

63. Potassium ferricyanid changes the color of ferric solutions to a brown but does not form a precipitate.

64. Potassium sulphocyanate gives to acidified ferric solutions a deep blood-red color without forming a precipitate. The color is due to the formation of ferric sulphocyanate, $Fe(SCN)_3$, which dissolves as a double salt with an excess of the KSCN. Hydrochloric acid does not decolorize it. The reaction may be used as an extremely sensitive test for iron. When soluble phosphates, borates or some organic acids are present the reaction may fail until the solution is strongly acidified with hydrochloric acid. The color is destroyed by mercuric chlorid.

65. Sodium carbonate or ammonium carbonate precipitates from ferric solutions reddish-brown, gelatinous ferric hydrate, $Fe(OH)_3$, CO_2 escaping.

66. Barium carbonate precipitates ferric compounds completely in the cold as basic salts.

67. Tannic or gallic acid forms a blue-black precipitate with ferric solutions.

Nickel, Ni.

Nickel dissolves slowly in hydrochloric and in dilute sulphuric acids, more readily in nitric acid. Nickelous salts of these acids are then formed. Most of the solutions of nickel are green.

A 2-per-cent. solution of $NiSO_4$ may be used for the reactions.

68. Ammonium sulphid in neutral or alkaline solutions precipitates black nickel sulphid, NiS, slightly soluble in

excess of the reagent, in the presence of ammonium hydrate, to a brownish solution. It does not dissolve in cold dilute hydrochloric acid but dissolves in aqua regia.

69. Ammonium hydrate gives at first a greenish precipitate of nickelous hydrate, $Ni(OH)_2$, which dissolves in a slight excess of the alkali to a blue liquid.

70. Sodium hydrate or potassium hydrate precipitates from nickel solutions the same compound, nickelous hydrate, $Ni(OH)_2$, which is insoluble in excess of the reagent. Sugar and some organic acids prevent this precipitation of nickel.

71. Potassium nitrite does not precipitate nickel from its solution in acetic acid.

Cobalt, Co.

Cobalt dissolves in acids like nickel with the formation of cobaltous salts. These are usually pink to red when they contain water of crystallization and blue when anhydrous. The solutions are red also.

Use a 2-per-cent. solution of $Co(NO_3)_2$ in the reactions.

72. Ammonium sulphid precipitates the cobalt from neutral or alkaline solutions as the black sulphid, CoS. It is insoluble in excess and in cold hydrochloric acid but dissolves, like the nickel sulphid, in aqua regia.

72. Ammonium hydrate gives a precipitate of a blue basic salt which turns green in the air. It dissolves in excess of the ammonia to a pink solution if the liquid is freed from oxygen and this, on standing in the air, becomes brown from oxidation. Organic compounds may prevent the precipitation.

74. Sodium hydrate or potassium hydrate produces the same basic salt as a precipitate. Upon boiling with an excess of the reagent this is converted into pink insoluble cobaltous hydrate, $Co(OH)_2$.

75. A considerable amount of potassium nitrite added to a cobalt solution, followed by acetic acid until it is strongly acid, and the whole allowed to stand in a warm place, precipitates the cobalt as $Co(NO_3)_3 \cdot 3KNO_2$, a yellow crystalline compound.

Directions for the Separation of Metals of Group III in the Absence of Phosphoric, Oxalic, Boric, Citric and Tartaric Acids.

The acidity of the solution containing the group should be neutralized by adding ammonium hydrate slowly, until a permanent precipitate begins to form. Then add about one-tenth its volume of ammonium chlorid and last ammonium sulphid until complete precipitation has been produced, but avoiding a large excess. Heat the mixture nearly to boiling and filter. If the original mixture contained groups IV and V they will be found in the filtrate. Otherwise it can be discarded. The precipitate contains the sulphids of nickel, cobalt, iron, manganese and zinc, with the hydrates of chromium and aluminum. Wash it with hot water.

Rinse the precipitate from the filter with about 15 cc. of dilute hydrochloric acid and let it stand five minutes in the acid, stirring occasionally. All the metals of the group with the exception of nickel and cobalt dissolve. The nickel and cobalt remain as black sulphids. If the insoluble residue is light colored or gray it may be only sulphur. Filter and wash.

Test the residue with the borax bead in the oxidizing flame. Cobalt gives a blue bead; nickel a purple, while hot, soon becoming brown. If the residue is so small that it cannot be removed from the paper, the part of the filter which contains it can be burned on the bead, when, after the complete oxidation of the carbon, the metal will be left to dissolve in the borax.

When only one of the two is present the colors will be clear but if both are contained in the bead, it may be necessary to separate them before they can be identified. To accomplish this dissolve the mixed sulphids in 2 cc. of warm aqua regia, filter and evaporate nearly to dryness under a hood, to remove the excess of acid. Dilute with water to 5 cc., add potassium nitrite and acidify strongly with acetic acid; warm gently and let it stand several hours. The cobalt gives a yellow precipitate. Filter and test the filtrate for nickel by sodium hydrate or ammonium sulphid. The former gives a green precipitate; the latter, a black one.

Boil, for a short time, the hydrochloric acid solution of iron, manganese, chromium, aluminum and zinc until it is freed from hydrogen sulphid as shown by the absence of odor or by its failure to discolor a paper dipped in lead acetate and held in the steam. Add to the hot liquid bromin water until it is colored yellow and bring to a boil. Make it alkaline with sodium hydrate, then add enough of the sodium hydrate to make a large excess.[1] Boil one minute and filter. The iron, manganese and chromium are precipitated as hydrates, and the zinc and aluminum are dissolved in the excess of the alkali. Dissolve a small portion of the precipitate in hydrochloric acid and test it for iron with potassium ferrocyanid. A blue color is produced. Place another portion of the precipitate on the platinum foil, add five times as much of a mixture of dry sodium carbonate and potassium nitrate and heat until it is thoroughly fused. If manganese is present the mass is a deep green. Chromium, in the absence of manganese, gives a yellow mass. In either case, to confirm the presence of chromium, place the foil in a test-tube, cover with water and heat to boiling.

[1] When sufficient alkali has been added the liquid has a soapy feeling if a drop is rubbed between the fingers.

Filter off the brownish residue if one is present and test the solution for chromium, after acidifying with acetic acid, by adding a few drops of lead acetate. A yellow precipitate of lead chromate is produced.

The solution of aluminum and zinc in excess of sodium hydrate should be slightly acidified with hydrochloric acid, then an excess of ammonium hydrate should be added and the liquid boiled for several minutes. Aluminum hydrate, a very flocculent white precipitate, is produced, which floats a long time in the liquid. Filter and, after dividing the filtrate into two parts, test one for zinc by a few drops of ammonium sulphid and warming. A flocculent white precipitate appears. From the second part, after it has been acidified with hydrochloric acid, potassium ferrocyanid precipitates zinc ferrocyanid, a very fine, white solid.

TABLE II.

OUTLINE OF SEPARATION OF THE METALS OF GROUP III IN ABSENCE OF PHOSPHORIC, BORIC, ETC., ACIDS.

To the solution add NH_4OH until, after shaking, there is a slight permanent precipitate. Then add NH_4Cl and a slight excess of $(NH_4)_2S$. Warm, filter and wash. The precipitate contains NiS, CoS, FeS, MnS, ZnS, $Cr(OH)_3$ and $Al(OH)_3$ if they were present in the original solution. Let it stand five minutes in cold dilute HCl, stirring frequently. All are dissolved except the sulphids of Ni and Co. Filter and wash.

<table>
<tr>
<td rowspan="2">If the insoluble residue is black apply the borax bead test.
A blue bead = Co.
A brown bead = Ni.
If a separation of the metals is desired dissolve the black residue in a little aqua regia, evaporate nearly to dryness, dilute with 5 cc. of water, add KNO_2, acidify with acetic acid and let it stand several hours, after warming. A yellow precipitate of potassium cobalt nitrite is formed. Filter and to the filtrate add NaOH and warm. $Ni(OH)_2$ a light green precipitate appears. With the same filtrate $(NH_4)_2S$ gives a black precipitate, NiS.</td>
<td colspan="2">The filtrate contains the chlorids of Fe, Mn, Zn, Cr, and Al.
Expel the hydrogen sulphid by boiling and add a slight excess of bromin water.
Then heat to boiling, make the liquid very strongly alkaline with NaOH, and boil one minute. Filter.</td>
</tr>
<tr>
<td>The precipitate contains $Fe(OH)_3$, $Cr(OH)_3$ and $Mn(OH)_2$.
Dissolve a small portion of the precipitate in HCl and test for Fe with $K_4Fe(CN)_6$. A dark blue color should appear.
Dry another portion of the precipitate on platinum foil, and thoroughly fuse with Na_2CO_3 and KNO_3.
Dark green K_2MnO_4 is formed.
Boil with a little water, filter, acidify with acetic acid and add lead acetate. Yellow $PbCrO_4$ is precipitated.</td>
<td>The filtrate contains Al and Zn.
Slightly acidify it with HCl, make it alkaline with NH_4OH and boil a minute. A light white precipitate is $Al(OH)_3$.
Filter and test the filtrate for Zn.
1. $(NH_4)_2S$ gives a white flocculent precipitate, ZnS.
2. $K_4Fe(CN)_6$ gives a fine white precipitate of $Zn_2Fe(CN)_6$ after acidifying with HCl.</td>
</tr>
</table>

Explanation of the Operations Used in the Separation of the Metals of Group III.

The object of the addition of ammonium hydrate is to neutralize any acid present, since this would otherwise decompose the ammonium sulphid and prevent the precipitation of the metals. Ammonium chlorid favors the complete precipitation of many of these, converting them

from a gelatinous to a more or less flaky consistency, which hastens the subsequent filtration. Warming likewise favors the precipitation and rapid filtration or the group. The precipitation should be accomplished chiefly by the ammonium sulphid, a large excess of which, together with ammonium hydrate, may cause a partial solution of the nickel sulphid. This gives the filtrate a brown color.

By the action of the hydrochloric acid the compounds of all the metals, with the exception of nickel and cobalt, are converted to chlorids which are soluble. The sulphids of these two metals are not soluble in cold dilute acid, although they are somewhat so if it is heated, or in the concentrated acid. Sulphur is set free from the ammonium sulphid by the action of ferric salts (60).

When the sulphids of the metals are dissolved in the acid hydrogen sulphid is formed and remains dissolved in the cold liquid. If it is not removed it would, as soon as the liquid becomes alkaline in the next operation, form sodium sulphid and this would change the iron, manganese and zinc compounds again into the sulphids instead of the hydrates. The zinc would remain with them, instead of being separated by the sodium hydrate.

Bromin water and other oxidizing agents change ferrous compounds to ferric in the presence of free acid. After this has been added it is necessary to use a large excess of the sodium hydrate, since by a small amount all five of the metals in the solution would be precipitated (33, 37, 42).

The fusion of the hydrates of iron, manganese and chromium does not change the appearance of the iron compound, but converts the manganese into a green substance which is insoluble in boiling water (49). At the same time the chromium hydrate is oxidized to a soluble yellow chromate (38).

If the aluminum solution is not made acid the base will not be precipitated by ammonium hydrate even if large amounts are present (33).

Separation of the Bases of Groups III and IV in the Presence of Phosphoric, Oxalic, Boric, Citric and Tartaric Acids or Their Salts.

(Capital and small letters are used for the identification of subdivisions of the groups—the former for solids, the latter for solutions.)

The metals of group III are ordinarily precipitated separately from those of group IV. If, however, the solution contains certain acids or their salts the metals of both groups are thrown down together by the reagents used for the precipitation of group III. The compounds whose presence causes this simultaneous precipitation of the two groups are phosphates, oxalates and borates, and also tartrates and citrates.[1] If it has been ascertained by testing that any of these are present the usual separation of the metals of groups III and IV should be modified in the following manner:

To the solution of the two groups add about one-tenth its volume of ammonium chlorid, make it faintly alkaline with ammonium hydrate and then add ammonium sulphid until no more precipitate (*A*) forms. Warm and stir the mixture until the precipitate begins to settle, filter and wash with water containing a few drops of $(NH_4)_2S$. Preserve the filtrate to test for bases of group IV which may be partially unprecipitated. The precipitate (*A*) may contain all the bases of groups III and IV, together with sulphur. Rinse it from the paper with about 15 cc. of dilute hydrochloric acid into a dish or beaker and stir it occasionally for five minutes. Filter and wash. There will remain insoluble (*B*) the sulphids of cobalt and nickel with sulphur.

[1] Fluorids and silicates act in the same nanner but are omitted here as being of less importance.

The remaining metals are dissolved and pass into the filtrate (*a*).

Nickel and cobalt sulphid, if present, are black; sulphur is grayish to yellow, burning with characteristic odor and blue flame if present in large quantity. To test for the nickel or cobalt dissolve the residue (*B*) in a borax bead with the aid of the oxidizing flame. Cobalt gives a deep blue color; nickel, a purple while hot, quickly passing to a brown. In cases of doubt, or where it is desirable to separate the metals, dissolve it in aqua regia and use potassium nitrite, as on page 53.

The hydrochloric acid solution (*a*) is to be used for the separation of the remaining bases. Boil it in a beaker or flask until the hydrogen sulphid is expelled, as shown by the absence of odor and by the failure of a strip of filter paper to turn brown after it has been moistened with lead acetate solution and suspended in the steam. If much sulphur separates during this boiling filter it out.

Mix about one-fourth of the solution (*a*) with dilute sulphuric acid. The sulphate of barium will be immediately precipitated (*C*), that of strontium, if much is present, or upon standing, and of calcium if this is present in concentrated solution, although the calcium in great part remains dissolved. After it has settled filter and wash, preserving the filtrate (*b*). If there is no precipitation by sulphuric acid calcium may nevertheless be in solution. To detect it here or after filtration from the sulphates of barium and calcium add three volumes of alcohol to (*b*) when the calcium sulphate will be precipitated if present. It can be dissolved in boiling water and tested with a few drops of ammonium oxalate which should give a fine white precipitate of calcium oxalate. To test for barium and strontium, if sulphuric acid caused a precipitation, place the washed, moist precipitate (*C*) in a porcelain dish, add about 10 cc. of

a 10-per-cent. solution of sodium carbonate, and boil gently for five minutes. Strontium sulphate, and calcium sulphate if it is present, are converted into carbonates, the barium sulphate being but little affected. Filter and wash. Pour over the precipitate (*D*) on the filter 10 cc. of hot acetic acid which will dissolve (*c*) the strontium carbonate but comparatively little of the barium salt. Wash the precipitate (*D*) discarding the wash-water. The barium may be confirmed by the appearance of a yellowish-green flame obtained from the insoluble residue (*D*) after it has been moistened with hydrochloric acid. To the acetic acid solution (*c*) add a few drops of potassium dichromate to precipitate the barium if any of this has been dissolved. This will be changed to yellow barium chromate. Filter when enough of the reagent has been added to give the supernatant liquid a yellow color. From the filtrate (*d*) precipitate the strontium by means of dilute sulphuric acid, adding it as long as the insoluble compound is formed and letting the mixture stand five minutes if no precipitate appears immediately. Filter and, after washing, confirm the strontium by moistening with hydrochloric acid and making the flame test with and without the blue glass (18).

To about a cubic centimeter of the hydrochloric acid solution (*a*) add enough bromin water to give a yellow color, boil and add a few drops of potassium ferrocyanid. A blue color is indicative of iron.

To the remainder of the hydrochloric acid solution (*a*), if iron has been found, add bromin water and boil as before. If iron is absent omit this step and proceed with the next operation, which is to remove from the solution (*a*) the phosphoric acid that may be present. This is effected by forming an insoluble compound of this with iron. To learn whether enough iron is present in the solution remove two or three drops and to these, in an evaporating dish,

add ammonium hydrate. If there is a yellowish-brown precipitate the amount of iron is sufficient; if it is nearly white add to the solution a few drops of ferric chlorid, and test a little of this with ammonium hydrate as before, repeating as many times as necessary to produce the yellow or brown precipitate. The free acid should now be nearly but not quite neutralized. This must be done by dropping in, with constant stirring, sodium hydrate solution until blue litmus paper is only slowly turned red. If too much has been used hydrochloric acid must be added until the proper reaction is attained. Now add an excess of barium carbonate. This is best done by shaking the solid reagent with water and using the milky mixture. Let this stand in the cold for half an hour, with frequent stirring. The liquid above the precipitate should be colorless if enough has been used. Then filter and wash. The precipitate (*E*) contains the hydrates of aluminum, chromium and iron, also the ferric phosphate and the excess of the barium carbonate. The filtrate (*e*) will contain the manganese and zinc, also the barium, strontium, calcium and magnesium, which may have been contained in the original substance.

Transfer the precipitate (*E*) from the filter to a porcelain dish, then boil it two minutes with about 10 cc. of sodium hydrate, cool and filter. This dissolves the aluminum, which passes into the filtrate. From this it can be precipitated by first acidifying with hydrochloric acid, then making faintly alkaline with ammonium hydrate and boiling for a minute in a beaker. The aluminum hydrate thus obtained is a white, very voluminous substance, which floats for a long time in the liquid.

To detect the chromium in the portion of the barium carbonate precipitate (*E*) which did not dissolve in sodium hydrate, dry it on platinum foil, then fuse thoroughly with a mixture of dry sodium carbonate and potassium nitrate.

The chromium produces a yellow mass which dissolves to a yellow solution in water and this, after acidifying with acetic acid, forms a bright yellow, insoluble lead chromate upon the addition of lead acetate.

To test for magnesium, zinc and manganese proceed as follows with the filtrate (*e*) from the barium carbonate precipitate. Acidify with dilute sulphuric acid, heating until the effervescence has ceased. This precipitates the barium, most of the strontium and possibly part of the calcium, and dissolves the manganese, zinc and magnesium. Filter and neglect the precipitate, since the bases contained in it have already been determined. To the filtrate add ammonium hydrate until it is alkaline, then ammonium sulphid. Manganese and zinc are precipitated as sulphids if they were contained in the mixture. Magnesium, with calcium and possibly some strontium, remains in the liquid (*f*). Filter and wash. Remove the precipitate (*F*) from the paper, dissolve it in a slight excess of hydrochloric acid, free it from hydrogen sulphid by boiling in an evaporating dish, and make it strongly alkaline with sodium hydrate. White manganous hydrate, soon turning brown, is precipitated, the zinc remaining in solution (*g*). Confirm the manganese by fusing it on the platinum foil with sodium carbonate and potassium nitrate, when a dark green mass results. The zinc may be separated from the solution (*g*) in sodium hydrate by the aid of a little hydrogen sulphid, which gives a white flaky precipitate of zinc sulphid.

To determine whether any magnesium is contained in the solution (*f*) from which the manganese and zinc sulphids have been filtered, add ammonium oxalate, which may give a white precipitate of calcium or strontium oxalate. Remove this by filtration, if it is formed, and to the filtrate add ammonium hydrate and sodium phosphate. A white crystalline precipitate indicates magnesium.

TABLE III.

OUTLINE OF SEPARATION OF THE METALS OF GROUPS III AND IV.

In the presence of phosphoric, oxalic, boric, tartaric and citric acids or their salts. To the solution add NH_4Cl, make alkaline with NH_4OH and precipitate with $(NH_4)_2S$. Warm, filter and wash. The precipitate contains NiS, CoS, FeS, MnS, ZnS, $Al(OH)_3$, and $Cr(OH)_3$, with Ba, Sr, Ca and Mg salts of the above acids, sometimes with S. Treat with HCl. If a residue remains filter and wash.

<table>
<tr>
<td rowspan="4">If the residue is black it may contain CoS and NiS. Test it with borax bead.
A blue bead indicates Co, a brown bead indicates Ni. To separate or distinguish these dissolve in aqua regia and use KNO_2 as on page 53.</td>
<td colspan="6">The filtrate contains Fe, Mn, Cr, Al, Zn, Ba, Sr, Ca and Mg. Expel the H_2S by boiling and divide the solution into three portions. To the first add dilute H_2SO_4. Filter and wash.</td>
</tr>
<tr>
<td rowspan="3">Precipitate contains $BaSO_4$ and $SrSO_4$ with possibly $CaSO_4$. Boil with Na_2CO_3, filter and wash. Insoluble residue contains $BaSO_4$ ($BaCO_3$?), $SrCO_3$ ($CaCO_3$?). Treat with acetic acid. Insoluble $BaSO_4$ remains. Confirm with flame test. From solution precipitate Ba with $K_2Cr_2O_7$, filter and add H_2SO_4; white precipitate of $SrSO_4$. Filter, wash and confirm by crimson flame.</td>
<td rowspan="3">Filtrate contains Ca. Mix a second portion with 3 volumes of alcohol. A white precipitate of $CaSO_4$. Dissolve in hot water and confirm by $(NH_4)_2C_2O_4$.</td>
<td colspan="4">Filtrate contains Fe, Mn, Cr, Al, Zn, Ca and Mg. Test a portion for Fe by $K_4Fe(CN)_6$. If iron is present, after oxidizing this with Br water add enough $FeCl_3$ to unite with the phosphoric and other disturbing acids, nearly neutralize the acidity and add $BaCO_3$. Allow to stand one half hour. Then filter and wash.</td>
</tr>
<tr>
<td colspan="2">Precipitate contains $Fe(OH)_3$, $Cr(OH)_3$, and $Al(OH)_3$. Boil with NaOH and filter.</td>
<td colspan="2">Filtrate contains Mn, Zn, Ca(Sr?) and Mg. Acidify with dilute H_2SO_4 and filter out the Ba and Sr if there is a precipitate. In the filtrate precipitate the Mn and Zn with NH_4OH and $(NH_4)_2S$. Filter.</td>
</tr>
<tr>
<td>Residue contains $Cr(OH)_3$. Fuse with Na_2CO_3 and KNO_3. Dissolve in water, add acetic acid and lead acetate. A yellow precipitate of $PbCrO_4$.</td>
<td>Filtrate contains Al. Acidify with HCl, add NH_4OH and boil. A light white precipitate of $Al(OH)_3$</td>
<td>Precipitate contains MnS and ZnS. Dissolve in HCl. Expel H_2S by boiling and add large excess of NaOH. $Mn(OH)_2$ is precipitated. Confirm by fusion with $NaCO_3$ and KNO_3 on Pt foil. Mn gives a green mass. From filtrate precipitate white, flaky ZnS by H_2S.</td>
<td>Filtrate contains (Ba, Sr?), Ca and Mg. With $(NH_4)_2C_2O_4$ precipitate all except Mg and remove by filtration. To the filtrate add $NaHPO_4$. Mg gives a white crystalline precipitate of NH_4MgPO_4.</td>
</tr>
</table>

Explanation of the Operations Used in the Separation of the Metals of Groups III and IV in the Presence of Phosphoric, Oxalic, Boric, Tartaric and Citric Acids and Their Salts.

The reason that it is necessary to modify the usual methods when these acids are contained in the solution is that the phosphates, oxalates, borates, tartrates and citrates of barium, strontium, calcium and magnesium are soluble in acids but not in neutral or alkaline liquids. They therefore will be precipitated with the third group as soon as ammonium hydrate has been added. Many of the explanations previously given regarding the analysis of groups III and IV will also be applicable here.

Nickel and cobalt can be easily separated from the rest of the precipitated bases because of the insolubility of their sulphids in dilute acid. From the solution thus obtained all the barium and most of the strontium are separated by conversion into sulphates by means of sulphuric acid which dissolves the other compounds. This does not make a clean separation between the alkali earth metals, though, since a part of the strontium may be left in solution or a part of the calcium may be changed to the insoluble sulphate if a large amount is present. Nevertheless it serves to distinguish them from each other. To give greater certainty of this the flame test should not be neglected. In the same way when the sulphates of barium and strontium are boiled with sodium carbonate some of the barium sulphate may become converted to the carbonate as the strontium sulphate is and thus pass with the strontium into solution.

The separation of the metals contained in the sulphuric acid filtrate is the same as in the separation where the metals of the alkaline earths are not present, except that alcohol is used to render more insoluble the calcium sul-

phate and after the bases of group III have been identified and the calcium removed the magnesium is precipitated by sodium phosphate in the usual manner.

Practical Exercises on Group III.

1. In a large test-tube mix together 3–4 cc. of the solutions of each of the metals of the group and separate them according to Table II.

2. In the same manner make analyses of the unknown mixtures of these metals which will be furnished by the instructors.

3. To solutions of these metals add those of group IV and sodium phosphate and make the analysis by the directions in Table III.

4. Examine the unknown mixtures furnished by the instructors to determine whether they contain any of the acids which would cause groups III and IV to precipitate together. If this is the case analyze the mixture by Table III.

Questions for Further Study on Group III.

In the fusion of chromium and manganese compounds with sodium carbonate and potassium nitrate what action has each of the latter reagents? What is the action of the Pb_3O_4 and nitric acid in the production of the red color from manganous compounds. Would ferrous or ferric salts be formed when iron is dissolved in hydrochloric acid? in dilute sulphuric acid? in concentrated nitric acid? Which will the more easily dissolve iron, concentrated or dilute sulphuric acid? What are some of the pharmaceutical preparations of iron from which ammonium hydrate would fail to produce a precipitate? What is the valence of the iron in ferrocyanid and ferricyanid? For what is ferrous carbonate used in medicine and what means is then adopted to prevent its oxidation? Is the rapidity of oxidation of ferrous compounds modified by the presence

or absence of moisture? What pharmaceutical preparations would be incompatible with iron compounds because of their containing tannic or gallic acid? What compounds of the alkali metals are chemically incompatible with salts of this group because of the resulting insoluble compounds? What can be used to prevent this precipitation? What chemical reagents can be employed to convert ferrous into ferric compounds? What application is made of the mutual decomposition of alum and an alkaline carbonate?

GROUP II.

Arsenic, antimony, tin, gold, platinum, mercury (ic compounds), lead, bismuth, copper, cadmium. Salts of these metals are precipitated from their acid solutions by hydrogen sulphid. For convenience they may be divided into two divisions: (A) Those of which the sulphids are insoluble in yellow ammonium sulphid, — mercuric compounds, lead, bismuth, copper and cadmium, and (B) those of which the sulphids are soluble in yellow ammonium sulphid, — arsenic, antimony, tin, gold and platinum.

Division A.

The sulphids of this division do not form soluble sulpho-salts with the alkaline sulphids and are consequently insoluble in these reagents. Their oxids, hydrates, carbonates, phosphates, arsenates, arsenites and iodids as well as sulphids are insoluble in water.

Copper, Cu.

The metal is practically insoluble in dilute sulphuric or hydrochloric acids but dissolves readily in nitric acid. Its soluble compounds are poisonous.

For the reactions a 2-per-cent. solution of $CuSO_4$ may be used.

76. Hydrogen sulphid or ammonium sulphid gives a brownish, nearly black, precipitate of copper sulphid,

CuS. It dissolves in hot nitric acid, also in solutions of potassium cyanid.

77. Sodium hydrate or potassium hydrate, with copper solutions, forms the light blue, insoluble, cupric hydrate, $Cu(OH)_2$, which is decomposed by boiling into black cupric oxid, CuO, and water. The presence of some organic compounds like glycerin, sugar and salts of tartaric and some other organic acids prevents the precipitation of copper by the sodium or potassium hydrate but instead it forms a deep blue solution. If one of the reducing sugars, like glucose, is present this, by boiling, reduces the cupric to a cuprous compound and yellow or reddish cuprous oxid is precipitated.

78. Ammonium hydrate in small amounts forms a bluish green precipitate, but this dissolves easily in an excess of the reagent to a deep blue solution which contains $(NH_3)_4$, $CuSO_4$. The addition of KCN decolorizes the liquid.

79. Soluble carbonates precipitate basic cupric carbonate which dissolves in excess of the ammonium carbonate.

80. Potassium ferrocyanid gives a precipitate of reddish-brown cupric ferrocyanid, $Cu_2Fe(CN)_6$, insoluble in dilute acids.

81. Metallic iron or zinc precipitates reddish metallic copper which collects on the metal.

82. Cupric chlorid gives a light blue color to the Bunsen flame; most other copper compounds give an emerald green.

Bismuth, Bi.

Bismuth will dissolve in nitric acid, forming the nitrate, and is not easily attacked by other acids. The soluble salts are decomposed by a large quantity of water, the bismuth being precipitated as a basic salt, and most of the acid being set free.

Use for the reactions a 2-per-cent. solution of $Bi(NO_3)_3$.

83. Hydrogen sulphid or ammonium sulphid precipitates black bismuth sulphid, Bi_2S_3, soluble in nitric acid.

84. The alkaline hydrates precipitate $Bi(OH)_3$, a white bulky solid, insoluble in excess.

85. A bismuth solution, free from a large amount of nitric acid, after dilution with ten to twenty times its volume of water forms a precipitate of a white basic salt. Boiling or the addition of a few drops of hydrochloric acid favors the precipitation.

$$Bi(NO_3)_3 + H_2O = BiONO_3 + 2HNO_3.$$

86. Stannous chlorid added to a solution of bismuth previously made alkaline by sodium hydrate reduces the bismuth to the black oxid, Bi_2O_2. This test can also be applied to many of the solid compounds.

$$2Bi(NO_3)_3 + SnCl_2 + 10NaOH = Bi_2O_2 + 6NaNO_3 \\ + 2NaCl + Na_2SnO_3 + 5H_2O.$$

87. Potassium dichromate produces a yellow precipitate of bismuth chromate, $Bi_2(CrO_4)_3$, which is soluble in nitric acid and insoluble in sodium hydrate.

88. Sodium carbonate precipitates white basic bismuth carbonate, or subcarbonate.

$$2Bi(NO_3)_3 + 3Na_2CO_3 + H_2O = (BiO)_2CO_3.H_2O \\ + 6NaNO_3 + 2CO_2.$$

Cadmium, Cd.

Cadmium dissolves in nitric, hydrochloric or dilute sulphuric acid with the formation of the corresponding salts.

A 2-per-cent. solution of $Cd(NO_3)_2$ may be used for the reactions.

89. Hydrogen sulphid or ammonium sulphid precipitates from cadmium solutions bright-yellow cadmium sulphid, CdS, which dissolves in nitric acid but not in potassium cyanid or alkaline sulphids.

90. The hydrates of sodium, potassium or ammonium give a precipitate of white cadmium hydrate, $Cd(OH)_2$, which is soluble in an excess of the last-named reagent.

91. Soluble carbonates precipitate white cadmium carbonate, insoluble in excess.

Mercury.

Mercury cannot be dissolved in hydrochloric acid. In cold, dilute nitric acid it dissolves to mercurous nitrate, $HgNO_3$; in hot, concentrated nitric acid it also dissolves, forming then mercuric nitrate, $Hg(NO_3)_2$. Salts of mercury volatilize upon heating, either without or with decomposition. All the soluble compounds are poisonous.

Mercuric Compounds, Hg''.

For the reactions a 2-per-cent. solution of $Hg(NO_3)_2$ may be employed.

92. Hydrogen sulphid or ammonium sulphid with mercuric solutions forms a white precipitate, if a very small amount of the reagent is used. As the reagent is increased the color changes to yellow, then brown, and, finally, black, insoluble mercuric sulphid, HgS, is formed. This is insoluble in yellow ammonium sulphid, also in nitric or hydrochloric acids when used singly. It does, however, dissolve easily in aqua regia.

93. Sodium hydrate or potassium hydrate, also the carbonates of these metals, produce a yellow precipitate of mercuric oxid, HgO. With only a small amount of the reagent a brownish basic salt is formed.

94. Ammonium hydrate precipitates white mercuric ammonium chlorid, NH_2HgCl.

$$2HgCl_2 + 2NH_4OH = NH_2HgCl + NH_4Cl + 2H_2O.$$

95. A few drops of stannous chlorid, in the presence of HCl, forms with mercuric salts a white precipitate of mercurous chlorid, HgCl.

$$SnCl_2 + 2HgCl_2 = SnCl_4 + 2HgCl.$$

If more of the stannous chlorid is added the white precipitate is changed to gray metallic mercury which only very slowly collects into large globules.

$$SnCl_2 + 2HgCl = SnCl_4 + Hg_2.$$

Other reducing agents produce HgCl, or, if strong, gray mercury in a similar manner.

96. A strip of sheet copper in a solution of mercury acidified with hydrochloric acid (but free from nitric acid) precipitates the mercury as a gray film of the metal on the surface of the copper. By rubbing with a cloth or the finger this becomes a bright, white copper amalgam. If the strip is inserted in a narrow test-tube and this is heated the mercury is volatilized and collects as a gray ring in the cool part of the tube. When examined with the microscope it is seen to be composed of globules of the metal. When these are rubbed with a glass rod they collect into larger globules. If a single crystal of iodin is dropped into the tube and this then gently warmed the metal is converted into the bright scarlet iodid, HgI_2. Zinc and iron, like copper, set free the mercury from the chlorid.

97. Potassium iodid, or other soluble iodids, with mercuric solutions form a red precipitate of mercuric iodid, yellow at first but soon becoming scarlet. It is soluble in excess of either potassium iodid or mercuric chlorid.

98. Dry compounds of mercury if mixed with dry sodium carbonate and heated in a matrass are decomposed, the mercury appearing in globules in the upper part of the tube.

99. Besides the above reagents many animal and vegetable substances form insoluble compounds with mercuric solutions, *e. g.*, albumin, alkaloids, extractive matters and a great number of others.

Division B.

The sulphids of this division unite with sulphids of the alkalies to form soluble compounds which are called sulpho-salts. These can be decomposed by acids, hydrogen sulphid being set free and the metals reprecipitated as sulphids.

Arsenic, As.

Metallic arsenic dissolves in dilute nitric acid to arsenous acid, and in concentrated nitric acid to arsenic acid. It is insoluble in hydrochloric and dilute sulphuric acids. Almost all its compounds are poisonous.

Dry Reactions of Arsenic and its Compounds.

100. Metallic arsenic volatilizes when heated, giving a garlic odor. If the heating is done in a matrass the metal is deposited upon the upper, cool part of the tube as a coating with a metallic luster. When in a rather thick layer it appears black by transmitted light, but it is of a brown shade when only a minute amount is present.

101. If a small fragment of the metal is placed in the middle of a narrow glass tube a few inches in length and open at both ends and is then heated over the Bunsen flame, holding the tube obliquely, the arsenic is oxidized and the white crystalline As_2O_3 is deposited in the upper part.

102. Arsenous oxid, As_2O_3, if heated in a matrass, sublimes without an odor, and is deposited upon the cooler part of the tube in octahedral or tetrahedral (eight-sided or four-sided) crystals. Their shape can be plainly seen with a microscope. The best crystals are obtained by having the upper part of the tube slightly warmed so as to prevent too rapid a deposition of the oxid.

103. Arsenous oxid when volatilized over glowing charcoal is reduced to the metal. This can be demonstrated by drawing out the closed end of a small matrass to a rather narrow point and, after it has cooled, placing a fragment

of the oxid in the end, with a splinter of charcoal above it. Heat the charcoal to redness first, then gradually heat the arsenic compound. A dark mirror of arsenic appears in the upper part of the tube. Some other compounds of arsenic will give the same result, but not all of them.

104. Arsenic sulphid and some of the arsenic compounds which are not reduced to the metallic form by charcoal alone, will be thus changed by mixing with sodium carbonate and potassium cyanid, both previously thoroughly dried, and heating in the matrass. The mirror appears as before.

Reactions of Compounds of Arsenic in Solution.

In making the reactions of the soluble compounds of arsenic we may consider them as belonging to two classes, first those in which the arsenic has the positive position, as it does in the halogen compounds, and, secondly, the arsenous and arsenic acids and their salts (arsenites and arsenates) where the arsenic is found in the negative part or acid radical. Some reactions will be common to all compounds; others will give different results with the different classes.

105. Arsenous oxid is soluble in water, though with difficulty. When so dissolved it forms the weak acid, H_3AsO_3, arsenous acid. It dissolves in hydrochloric acid to arsenous chlorid, $AsCl_3$. Sodium hydrate or potassium hydrate dissolves arsenous oxid easily with the formation of the arsenites of these metals. Nitric acid and also aqua regia convert it into soluble arsenic acid, H_3AsO_4.

General Reactions of Soluble Arsenous Compounds (As''').

Use a 1-per-cent. solution of $AsCl_3$, As_2O_3, or K_3AsO_3.

106. Hydrogen sulphid with neutral or alkaline solutions gives no precipitate, but upon the addition of hydrochloric acid it precipitates the arsenic as bright yellow

arsenous sulphid, As_2S_3. This is soluble in the alkaline hydrates, carbonates or sulphids, but not in hydrochloric acid. Boiling nitric acid dissolves it after converting it into arsenic acid.

107. From acid solutions, ammonium sulphid, $(NH_4)_2S$, precipitates the same compound, As_2S_3, soluble in excess as ammonium sulpharsenite, $(NH_4)_3AsS_3$. From this solution acids precipitate As_2S_3 again.

Reactions of Arsenous Acid and Arsenites.

Use a 1-per-cent. solution of As_2O_3 or K_3AsO_3.

108. Silver nitrate in neutral solutions of an arsenite forms yellow silver arsenite, Ag_3AsO_3, soluble both in excess of ammonia and nitric acid. This reaction is concealed by the presence of any acid or salt which precipitates silver nitrate, such as hydrochloric acid or the chlorids. A convenient way to make the reaction is to first acidify the arsenous solution with nitric acid in a narrow test-tube, then, after adding a few drops of silver nitrate, to slant the tube and pour ammonia down the side carefully so as to prevent the liquids from mixing. The precipitate appears in the neutral zone between them.

109. Copper sulphate in neutral solutions in the same way produces yellowish-green cupric arsenite, $CuHAsO_3$. It dissolves in either ammonium hydrate or nitric acid.

110. Salts of most metals except those of the alkalies form insoluble arsenites in neutral solutions.

General Reactions of Arsenic Compounds (As^{v}).

Use a 1-per-cent. solution of Na_2HAsO_4.

111. Hydrogen sulphid gives no precipitate in neutral or alkaline solutions of arsenates. If they are acidified it slowly reduces them to arsenous compounds, then precipitates them as arsenous sulphid, As_2S_3. Warming hastens the reduction and precipitation, but several hours are required

for its completion—sometimes twenty-four. Sulphur is precipitated at the same time.

112. Ammonium sulphid produces no precipitate, although the soluble ammonium sulpharsenate $(NH_4)_3AsS_4$, is formed. When this is acidified with hydrochloric acid yellow arsenic sulphid, As_2S_5, is precipitated.

Reactions of Arsenic Acid and Arsenates.

Use a 1-per-cent. solution of Na_2HAsO_4.

113. Silver nitrate produces in neutral solutions of arsenates, a reddish-brown precipitate of silver arsenate, Ag_3AsO_4, soluble in dilute nitric acid and ammonium hydrate. The reaction may be made in the same manner as in 108.

114. Copper sulphate, from neutral solutions precipitates greenish-blue cupric arsenate, $CuHAsO_4$, soluble in ammonium hydrate or nitric acid.

115. Magnesia mixture (magnesium sulphate with ammonium chlorid and ammonium hydrate; it must be a clear solution and not cloudy), in solutions of an arsenate, forms white crystalline ammonium magnesium arsenate It dissolves easily in acids.

116. Soluble salts of most metals except the alkali metals form, in neutral liquids, insoluble arsenates.

General Reactions of Arsenous and Arsenic Compounds.

Use a 1-per-cent. solution of any compound of arsenic.

117. From solutions of arsenic, strongly acidified with hydrochloric acid and warmed with strips of sheet copper, copper arsenid is precipitated which forms a dark-gray film on the surface of the copper. With very dilute solutions this can be accomplished by placing the solution with the copper in a test-tube and letting it stand half an hour in a beaker of boiling water. If then the copper is removed, washed with water, dried and heated in a small

open tube (101) the arsenic is oxidized to As_2O_3, which is deposited in microscopic crystals. The copper remains black from the formation of its oxid (Reinsch's test). This test is very sensitive and is not prevented by the presence of organic matter.

118. Acidify 3–4 cc. of arsenic solution with pure hydrochloric or sulphuric acid, add a small piece of zinc (about one gram) that is known to be free from arsenic, cover the mouth of the tube with several thicknesses of filter paper upon the upper one of which has been put a drop of *saturated* silver nitrate solution. Let the tube stand where it is protected from a bright light and from hydrogen sulphid. After a time, varying with the amount of arsenic present, the spot on the paper becomes yellow with a brown or black margin. The addition of water changes it to black. The yellow compound is $Ag_3As, 3AgNO_3$. This is produced by the action of the AsH_3— formed by the nascent hydrogen and the soluble arsenic compound — and the silver nitrate. Water decomposes it, setting free metallic silver. (Gutzeit's test.)

$$Ag_3As,3AgNO + 3H_2O = 6Ag + H_3AsO_3 + 3HNO_3.$$

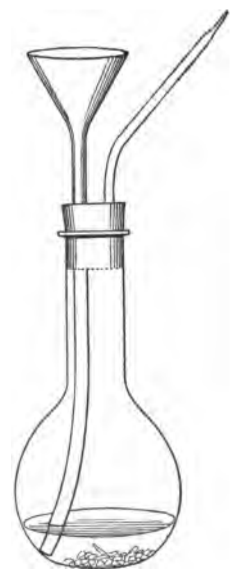
This test is a very sensitive one.

119. If sodium hydrate or potassium hydrate is substituted for the acid, the operation being otherwise performed in the same way, except that the solution may be slightly warmed, the same result appears (Fleitmann's test). This reaction is of value in distinguishing between arsenic and antimony.

120. To 3–4 cc. of an arsenic solution add an equal volume of concentrated hydrochloric acid and half a gram of metallic tin, granulated or in the form of foil. Upon warming for some time a brown color or precipitate of arsenic is produced (Bettendorf's test).

121. Nascent hydrogen converts arsenic compounds into gaseous hydrogen arsenid, or arsine, AsH_3. This can be decomposed either by heating or by cooling the flame of the burning gas, the arsenic being deposited as a dark mirror-like coating on cold objects. This is the basis of Marsh's test. For making this many forms of apparatus have been proposed. The simplest of these consists of a small flask (200–300 cc.) fitted with a doubly perforated stopper, one of rubber being preferable to cork. Through one hole a funnel-tube (a funnel with a piece of rubber tubing slipped over the stem answers for this) passes nearly to the bottom of the flask. The other is provided with an exit tube of difficultly fusible glass which does not project into the flask and of which the outer end is drawn out to a small point. Into this apparatus is put 5–10 grams of pure granulated zinc, the stopper is inserted and dilute sulphuric acid (one to eight), is poured in through the funnel tube. The hydrogen is allowed to escape until it is judged that all the air has been expelled before the gas is ignited. If there is any doubt of this a towel should first be loosely wrapped about the flask to avoid any flying fragments of glass if there is any explosion. Notice the color of the hydrogen flame, then hold in it a cold porcelain dish moving it about so as to prevent its becoming excessively heated. If the zinc and acid are both free from arsenic there will be no discoloration of the porcelain. Now pour into the hydrogen flask a few drops of the solution to be

FIG. 11.



A simple form of generator for Marsh's test.

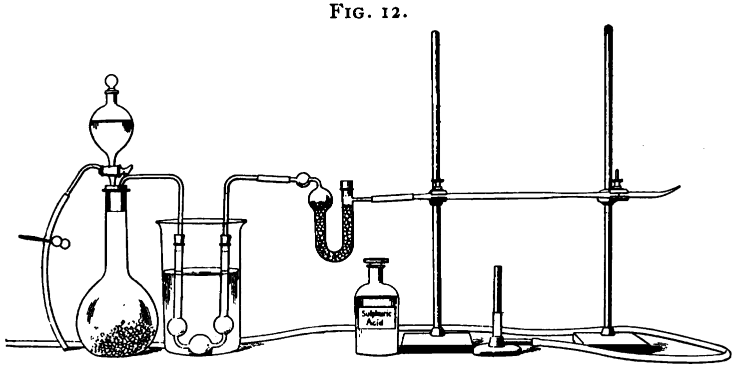
tested for arsenic, avoiding as far as possible the introduction of air with it. The color of the flame soon changes to a bluish-white and upon the dish there will be deposited a brownish or black mirror of arsenic. The gas should not be allowed to escape into the room unburned after the arsenic compound is present since the hydrogen arsenid is extremely poisonous. Apply the following tests to the arsenic mirror.

(*a*) Drop upon it a little of a solution of chlorinated lime (calcium hypochlorite). The mirror dissolves.

(*b*) Add a drop of strong nitric acid. This also dissolves the arsenic. Carefully evaporate this solution to dryness, without heating to a high temperature. Moisten it with a drop of silver nitrate. A brick-red color will be produced.

(*c*) Add to the mirror a few drops of ammonium sulphid. The arsenic is dissolved and the solution, if evaporated to dryness, leaves a yellow residue of arsenic sulphid.

FIG. 12.



Apparatus for the detection of a minute amount of arsenic by Marsh's test.

Where the test is to be made more carefully, for minute amounts of arsenic, a somewhat larger generating flask is used (perhaps one liter), with more of the zinc. The funnel tube should be provided with a stop-cock to prevent the admission of air. The gas will contain moisture from the dilute acid, and to remove this should be passed first

through an empty U-tube cooled by suspension in water, then through a tube which is filled with lumps of dried calcium chlorid. The latter absorbs the moisture which is not condensed in the first tube. The dry gas now passes through a horizontal tube of glass which does not soften except at a very high temperature ("hard glass"). This tube is to be heated to redness with a Bunsen burner *after all air has been driven out of the apparatus.* Before introducing the arsenic solution, while the hydrogen is passing through it, the tube should be heated for half an hour to prove the purity of the reagents used. The presence of arsenic is denoted by a brown or black mirror in the part of the tube immediately beyond the flame. If the glass is at this place contracted to a small diameter the mirror is more evident. If any of the arsenic compound is not decomposed here, which is usually the case, it can be tested for in the flame at the pointed end of the tube by means of the cold porcelain, as described above. During the test the escaping gas should be burned at the end of the tube or passed into a solution of silver nitrate to prevent the hydrogen arsenid from escaping into the air. With silver nitrate it forms a precipitate of metallic silver (black) and dissolves in the liquid. In long operations it is advisable to provide a means of removing the exhausted acid without the admission of air. This may be effected by inserting through a third hole in the stopper a bent glass tube closed at the outer end by a clamped rubber tube. By opening the clamp and closing the exit tube for a second the liquid can be siphoned from the flask. Where very minute amounts of arsenic are sought the operation may last for several hours.

The arsenic mirror in the tube, when gently warmed in a slow stream of dry hydrogen sulphid, is converted into yellow arsenous sulphid. The reactions made with the mirror on porcelain can be applied here also.

By Marsh's test less than one one-hundredth of a milligram of arsenic in a cubic centimeter has been detected. It is interfered with or prevented by the presence of oxidizing agents, organic matter and the salts of some heavy metals like mercury.

122. Freshly precipitated ferric hydrate (61) removes arsenous acid or arsenites from their solutions, as can be seen by shaking an excess with the arsenical liquid, filtering and testing the filtrate for the arsenic. It has been converted into an insoluble basic salt. Magnesium hydrate or oxid acts in a similar manner.

123. The soluble hydrates and carbonates precipitate neither arsenous nor arsenic compounds.

Antimony, Sb.

The metal is of a white color with a bright luster and is very brittle. It does not dissolve in hydrochloric acid, but is soluble as a chlorid in aqua regia. Stong nitric acid changes it into a white metantimonic acid that is nearly insoluble in the nitric acid. Its soluble compounds, in large doses, are poisonous.

For the reactions a 1-per-cent. solution of $KSbOC_4H_4O_6$ may be used.

124. Hydrogen sulphid precipitates from acid solutions orange-red antimonous sulphid, Sb_2S_3. It is soluble in ammonium sulphid, as well as in the other alkaline sulphids, but is insoluble in ammonium carbonate. Boiling concentrated hydrochloric acid dissolves it but it is insoluble in dilute acids.

125. From faintly acid solutions ammonium sulphid precipitates the same orange-red antimonous sulphid but dissolves it in excess to ammonium sulphantimonate which, like the corresponding arsenic compound, is decomposed by acids with the precipitation of Sb_2S_5.

126. Metallic zinc precipitates from solutions which contain no nitric acid fine, black, metallic antimony. If, in an antimony solution containing an excess of hydrochloric acid, a piece of platinum foil is brought in contact with the zinc, the antimony is deposited as a dark-brown or black stain on the platinum. This can be removed by hot nitric acid but does not dissolve in hydrochloric acid.

127. With nascent hydrogen, in a Marsh's apparatus (121), the antimony is converted into hydrogen antimonid, SbH_3, a gas which is decomposed like the AsH_3 with the formation of an antimony mirror. It has these points of difference from arsenic:

(*a*) It is usually of a more sooty black, although this may not be evident where only a very small amount is present.

(*b*) In the tube of the Marsh's apparatus it is formed on both sides of the spot where the glass is heated, and is not so easily volatile as the arsenic.

(*c*) It does not dissolve in a solution of calcium hypochlorite.

(*d*) It dissolves in a drop of strong nitric acid but upon subsequent evaporation to dryness and moistening with silver nitrate solution it remains colorless.

(*e*) When warmed in a current of dry hydrogen sulphid gas it is changed into red or black antimonous sulphid.

(*f*) In ammonium sulphid it dissolves and upon evaporation to dryness the orange or red sulphid, Sb_2S_3, remains.

128. Many of the soluble antimony salts are decomposed by large quantities of water with the precipitation of basic salts. This is true of the chlorid, which is changed into the basic chlorid. It sometimes occurs also when antimony solutions are slightly acidified by hydrochloric acid. The precipitate dissolves in a larger amount of the acid or in tartaric acid and is prevented from appearing if the tartaric acid is added previously.

129. With Reinsch's test (117) antimony compounds give a dark coating on the copper but by heating in the open tube this forms amorphous Sb_2O_3 which can be distinguished from the arsenic compound by the aid of the microscope (102).

130. Gutzeit's test (118) gives immediately a black or brown stain of silver antimonid, Ag_3Sb, on the paper, not a yellow one.

131. Fleitmann's test (119) gives no result with antimony compounds.

132. Tannic acid with an antimony potassium tartrate solution forms a white precipitate of antimony tannate, soluble in tartaric acid.

With Bettendorf's test (120) the antimony compounds give no reaction.

Soluble hydrates and carbonates precipitate white antimonous hydrate, $Sb(OH)_3$.

Tin, Sn.

The metal dissolves in concentrated hydrochloric acid, forming stannous chlorid. Concentrated nitric acid changes it into a white compound, insoluble in excess. In concentrated aqua regia tin dissolves to stannic chlorid.

There are two series of tin compounds, the stannous and the stannic. The former are readily converted into the latter by oxidizing agents or by standing exposed to the air.

Stannous Compounds (Sn″).

Use a 2-per-cent. solution of $SnCl_2$ for the reactions.

133. Hydrogen sulphid in neutral or acid solutions precipitates stannous sulphid, SnS, a dark brown compound. It dissolves in boiling hydrochloric acid. It is insoluble in colorless ammonium sulphid but soluble in the yellow ammonium sulphid to a sulpho-stannate, $(NH_4)_2SnS_3$. From

this solution acids precipitate yellow stannic sulphid, SnS_2, mixed with sulphur.

134. Ammonium sulphid precipitates stannous sulphid.

135. Sodium hydrate or potassium hydrate precipitates white stannous hydrate, $Sn(OH)_2$, soluble in excess, from which solution boiling precipitates stannous oxid, SnO.

136. Ammonium hydrate also precipitates stannous hydrate, but does not dissolve it in excess.

137. Metallic zinc precipitates dark gray or black, spongy, metallic tin from solutions containing hydrochloric acid. If platinum foil is present it is not discolored.

138. Mercuric chlorid in hydrochloric acid solution gives a white precipitate of mercurous chlorid, HgCl, which turns black upon being made alkaline with ammonium hydrate.

Stannic Compounds (Sn^{iv}).

Use for reactions a 2-per-cent. solution of $SnCl_4$.

139. Hydrogen sulphid in excess precipitates from acid or neutral solutions yellow stannic sulphid, SnS_2. It dissolves in boiling hydrochloric acid and in the alkaline sulphids to a sulpho salt (133).

140. Ammonium sulphid gives the same, soluble in excess and reprecipitated unchanged by acids.

141. Zinc gives the same result as with stannous salts.

Gold, Au.

Gold is insoluble in nitric, hydrochloric or sulphuric acids. It dissolves in aqua regia or in other liquids where chlorin is set free forming the chlorid, $AuCl_3$, and also is soluble in potassium cyanid.

A very dilute solution of the chlorid may be used for the reactions.

142. Hydrogen sulphid precipitates solutions of gold as a dark brown auric sulphid, Au_2S_2, that is soluble in

alkaline polysulphids and in aqua regia, but not in single acids.

143. Ferrous sulphate precipitates from acid solutions metallic gold as a yellowish-brown powder.

$$2AuCl_3 + 6FeSO_4 + 3H_2SO_4 = Au_2 + 3Fe_2(SO_4)_3 + 6HCl.$$

144. Oxalic acid, $H_2C_2O_4$, also precipitates the metallic gold from its solutions.

$$2AuCl_3 + 3H_2C_2O_4 = Au_2 + 6HCl + 6CO_2.$$

The last two reagents precipitate the gold because of their power of reduction. Other reducing agents act in a similar manner.

145. Stannous chlorid containing a little stannic chlorid, $SnCl_4$, formed by partly oxidizing the stannous solution, gives with gold solutions a purple compound of varying composition, called the Purple of Cassius. It remains in suspension giving a purple color to the liquid.

146. Metallic zinc, iron, copper or mercury, as well as some other metals, will precipitate the gold in the dark, finely divided metallic form.

147. Ammonium hydrate, in concentrated gold solutions, forms a precipitate of reddish-yellow fulminating gold which, when dry, explodes violently by friction.

148. Compounds of gold are decomposed, the metal being precipitated, by organic matter, *e. g.*, by boiling with sugar.

149. Very minute quantities of gold, for example, a fraction of an ounce in a ton of ore, can be detected by extracting the metal from the finely powdered material by means of its own volume of tincture of iodin. It should be left in contact for some time to ensure an effective solution. If then a piece of absorbent white paper is dipped in the solution and afterwards dried and burned the gold will

color the ash purple. The test is more delicate if the paper is dipped and dried several times before ignition.

Platinum, Pt.

The metal is not soluble in single acids but it dissolves in aqua regia, although not so readily as does gold. This solution contains platinic chlorid, $PtCl_4$.

A 1-per-cent. solution of $PtCl_4$ may be used for the reactions.

150. Hydrogen sulphid in acid solutions precipitates slowly (best with the aid of heat) platinic sulphid, PtS_2. This is a nearly black compound, insoluble in single acids but soluble in alkaline polysulphids. From this, acids reprecipitate the sulphid. It is also soluble in aqua regia.

151. Ammonium chlorid or potassium chlorid precipitates from hydrochloric acid solutions a double salt—ammonium platinum chlorid, $PtCl_4$, $2NH_4Cl$, or potassium platinum chlorid, $PtCl_4$, $2KCl$. These are yellow crystalline salts, somewhat soluble in water and rendered less so when alcohol is present.

152. Metallic zinc or iron precipitates the platinum as spongy black metallic platinum.

153. Oxalic acid does not precipitate platinum solutions and ferrous sulphate does so only after long boiling. Some other organic substance, however, like sugar or alcohol, will decompose boiling alkaline solutions, the metal being thrown down as a fine, black powder—platinum black.

Directions for the Separation of the Metals of Group II.

If the solution does not contain free acid, make it acid by the addition of hydrochloric. Precipitate all the bases of the group with hydrogen sulphid. This may be done by allowing the gas to pass through the solution, or by the use of a solution of hydrogen sulphid in water until a

precipitate no longer appears. Warm and stir the liquid until the precipitate settles, then when the metals have been completely precipitated filter and wash. Groups III, IV and V pass into the filtrate. Group II is divided into two divisions, A and B, according to whether it is insoluble (A) or soluble (B) in yellow ammonium sulphid. Scrape the precipitate[1] from the filter or rinse it off with the aid of 15 cc. of yellow ammonium sulphid into a small porcelain dish. Heat gently, but not to boiling and keep it at this temperature for five minutes, stirring often. Filter and wash, discarding the wash water. If the precipitate has a tendency to pass through the filter this may be prevented by warming with 5 cc. of ammonium chlorid solution.

Division A — Sulphids Insoluble in Yellow Ammonium Sulphid.

The precipitate, obtained by saturating the acidified solution with hydrogen sulphid, contains the sulphids of mercury, lead, bismuth, copper and cadmium.

After the precipitate has been well washed rinse it from the paper with 10 cc. of dilute nitric acid and boil. The sulphids are all dissolved with the exception of the black mercuric sulphid which remains as a heavy sediment. A part of the lead sulphid may be oxidized to lead sulphate, an insoluble, white, heavy powder. Sulphur may also be present as a grayish, floating powder. Remove the mercuric sulphid from the paper and dissolve it in 5 cc. of aqua regia (three volumes of hydrochloric and one volume of nitric acid), warming somewhat but not boiling. Filter off the sulphur and test the filtrate with a few drops of

[1] Instead of at first treating the whole precipitate with ammonium sulphid it is better to test a small portion thus to learn if B is present. If it is, treat the whole in the same manner; if not, proceed directly to the examination for A. If it dissolves completely A is absent.

stannous chlorid. The mercury is precipitated as a white chlorid which becomes gray with an excess of the tin solution or after heating.

The solution of lead, bismuth, copper, and cadmium should be evaporated nearly to dryness under a hood, then diluted to 10 cc. with water and tested for lead by adding dilute sulphuric acid (avoiding a large excess) and half a dozen drops of alcohol. Lead sulphate, a fine, white, heavy powder is thrown down. It should be allowed to settle before filtering and, if necessary, a little more alcohol added to insure a complete precipitation. Filter and wash. The lead may be confirmed by the solubility of the washed sulphate in sodium hydrate and the blackening of this solution by the addition of ammonium sulphid.

To the filtrate from the precipitated lead sulphate, which contains nitrates of bismuth, copper and cadmium, add ammonium hydrate until it smells strongly of this reagent. The bismuth is precipitated as a white flocculent hydrate while the copper and cadmium dissolve in excess, the former giving a deep blue solution. Filter, wash, and confirm the bismuth by the addition of a few drops of sodium hydrate and as much stannous chlorid, to the substance on the paper, when the compound turns black.

If a blue color indicates copper in the filtrate from the bismuth, acidify one half and confirm the copper by potassium ferrocyanid which produces a reddish-brown precipitate. To the remainder add potassium cyanid until the blue color disappears, then precipitate the bright yellow cadmium sulphid by hydrogen sulphid. If no blue color is present the copper is probably absent in which case the potassium cyanid may be omitted and the whole filtrate from the bismuth may be tested for cadmium.

Division B — Sulphids Soluble in Yellow Ammonium Sulphid.

This contains the sulphids of arsenic, antimony, tin, gold and platinum. Acidify the filtrate with hydrochloric acid. The sulphids of three bases are precipitated in curdy masses. If the precipitate is fine and nearly white and settles very slowly it is only sulphur and may be neglected. Otherwise filter and wash, adding ammonium chlorid as above if the filtrate is not clear.[1] From the precipitate which contains the sulphids of all the metals of Division B, dissolve the arsenic sulphid by digesting several minutes with about 10 cc. of ammonium carbonate, then filter. The arsenic can be detected in this solution after acidifying, by applying to the liquid which contains the sulphid in suspension Gutzeit's (118) or Reinsch's (117) tests.

The well-washed precipitate should have the water removed from it as far as possible by draining and pressing, then after removal from the paper is to be warmed in concentrated hydrochloric acid for several minutes. This should be done under a hood and the acid must not be allowed to boil violently. The sulphids of antimony and tin dissolve, and those of gold and platinum remain, mixed with some sulphur and possibly a part of the arsenic sulphid.

After filtering pour the filtrate into a dish, add a few fragments of zinc and immediately bring a piece of platinum foil into contact with this. If antimony is present it will make a brown or black stain on the foil to which it adheres very firmly. The tin is precipitated in the metallic form but nearly black in color and so heavy that it quickly settles to the bottom. Let the action proceed until it seems certain that all the antimony and tin are precipi-

[1] As the filtrate is not to be used it may, for economy of time, be decanted without filtration.

tated, then wash the tin by decantation and dissolve it in one or two cubic centimeters of warm concentrated hydrochloric acid. This solution when added to mercuric chlorid precipitates white mercurous chlorid, which turns black if the liquid is made alkaline with ammonia. If the stannous chlorid is in excess it sets free gray metallic mercury from the mercurous chlorid.

The antimony can be confirmed, if thought desirable, by warming the coated foil in 2–3 cc. of yellow ammonium sulphid in a test-tube, then evaporating to dryness. Orange-red antimonous sulphid remains.

The remaining precipitate from which the sulphids of arsenic, antimony and tin have been dissolved by ammonium carbonate and hydrochloric acid will be dark colored if it contains the sulphid of gold or platinum. Otherwise it will consist of sulphur with possibly some arsenic sulphid that the ammonium carbonate did not completely dissolve. If it is dark in color, warm it with aqua regia to dissolve the gold and platinum, filtering if solution is not complete. Test half the filtrate for gold with a mixture of stannous and stannic chlorids (Purple of Cassius, 145). From the other half, precipitate the yellow, crystalline ammonium platinic chlorid with NH_4Cl, using a rather strong solution. Confirm this by examination with the microscope (151).

Explanation of the Separation of the Metals of Group II.

If group I has previously been removed from the solution it will contain hydrochloric acid, otherwise this must be added, partly to favor the precipitation of some of the sulphids in this group, partly to prevent a precipitation of some of those of group III. A large amount of hydrogen sulphid will be necessary because the solution cannot be

made concentrated and the gas precipitates the metals slowly.

Arsenic, antimony and tin sulphids are all converted into soluble sulpho-salts by the ammonium sulphid. In the case of stannous sulphid the yellow or polysulphid is necessary. This is made by dissolving sulphur in the colorless ammonium sulphid, when one or more atoms of sulphur are added

Table IV.

Outline of the Separation of the Metals of Group II.

From the acidified solution precipitate with H_2S. The precipitate contains all the bases as sulphids. Filter and wash. Warm the precipitate in yellow ammonium sulphid. Filter and wash. The filtrate contains the sulphids of As, Sb, Sn, Au and Pt (Division B). The precipitate contains HgS, PbS, Bi_2S_3, CuS and CdS (Division A).

DIVISION A.

After the precipitate, formed by H_2S, has been washed boil it with HNO_3, and filter.

<table>
<tr><td rowspan="3">A black insoluble residue is HgS, often mixed with sulphur and $PbSO_4$. Warm it with aqua regia, and after filtering add $SnCl_2$. White HgCl is precipitated, changed to gray Hg with excess of the reagent.</td><td colspan="4">The solution contains the nitrates of Pb, Bi, Cu, and Cd. Evaporate it nearly to dryness under a hood. Dilute with water and precipitate the Pb with dilute H_2SO_4 and a few drops of alcohol, if necessary for complete precipitation. Filter and wash.</td></tr>
<tr><td rowspan="2">The precipitate is $PbSO_4$. Dissolve in NaOH and add to the solution H_2S. Black PbS is produced.</td><td colspan="3">The filtrate contains Bi, Cu, and Cd. Add NH_4OH in excess and, if there is a precipitate, filter.</td></tr>
<tr><td>$Bi(OH)_3$ is the precipitate. After it has been washed moisten it on the paper with NaOH then with $SnCl_2$. It turns brown or black.</td><td>The presence of Cu in the solutions is indicated by the blue color. Acidify one part and add $K_4Fe(CN)_6$. $Cu_2Fe(CN)_6$, a reddish brown compound appears.</td><td>To the other part add KCN until it is colorless, then H_2S. Yellow CdS is precipitated. In absence of Cu omit KCN.</td></tr>
</table>

DIVISION B.

Acidify the filtrate slightly with HCl. The As_2S_3, Sb_2S_3, SnS_2, Au_2S_3, and PtS_2 are precipitated with fine white sulphur. Filter and wash, discarding the filtrate. Warm the mixed sulphids for several minutes in a test-tube with $(NH_4)_2CO_3$. Filter and wash.

<table>
<tr>
<td rowspan="2">The solution contains the As. Acidify with HCl and apply Gutzeit's or Reinsch's test.</td>
<td colspan="2">The insoluble residue contains Sb_2S_3, SnS_2, Au_2S_3 and PtS_2. As far as possible remove water, place in a porcelain dish and warm under a hood with concentrated HCl. Filter.</td>
</tr>
<tr>
<td>The filtrate contains $SbCl_3$ and $SnCl_2$. Add a little Zn, and touch it with a Pt foil. The Sb makes a brown deposit on the Pt. The Sn is precipitated as a heavy black powder. Wash this by decantation and dissolve in concentrated HCl. A few drops of $HgCl_2$ gives a white precipitate, HgCl (blackened by NH_4OH), or gray Hg.
If the foil is rinsed, then warmed in $(NH_4)_2S_x$, the Sb is dissolved and after evaporation to dryness leaves orange-red Sb_2S_3.</td>
<td>The insoluble part contains only S and (possibly) As_2S_3 if it is light-colored. If Au_2S_3 or PtS_2 is present it is dark-colored. In the latter case warm it with aqua regia and filter out any insoluble residue. The filtrate contains $AuCl_3$ and $PtCl_4$. Divide it into two portions. To one add stannous and stannic chlorids. A purple color indicates gold. To the other add NH_4Cl. Yellow precipitate of $PtCl_4$, $2NH_4Cl$.</td>
</tr>
</table>

to the molecule, forming $(NH_4)_2S_x$ where x = two or more. The tin is changed to a stannic compound when it dissolves.

$$SnS + (NH_4)_2S_2 = (NH_4)_2SnS_3.$$

Acidifying decomposes the sulpho-salt and precipitates the tin as a stannic, not a stannous, sulphid.

$$(NH_4)_2SnS_3 + 2HCl = SnS_2 + 2NH_4Cl + H_2S.$$

In the digestion of the mixed groups with yellow ammonium sulphid boiling must be prevented because this would decompose the ammonium sulphid.

Sulphur is always precipitated, white because of its fineness, when a polysulphid is acidified.

$$(NH_4)_2S_2 + 2HCl = 2NH_4Cl + H_2S + S.$$

Explanation of the Separation of the Metals of Group II, Division A.

The sulphids of copper, bismuth and cadmium dissolve in boiling nitric acid, forming nitrates, and lead[1] does so in part, but may be partly oxidized to insoluble lead sulphate. This remains with the mercuric sulphid which does not dissolve in a single acid. The lead compound does not become soluble by the action of aqua regia but the mercuric sulphid is changed to the chlorid. The action of the tin chlorid is as described in 95.

The portion of the lead which went into solution with the other metals can be precipitated as the sulphate but since the presence of much free nitric acid will to some extent prevent this, thus leaving some of the metal to interfere with future tests, it is better to remove the acid. To accomplish this the evaporation must be carried so far that but a very small bulk remains as the acid is driven off only after the water, in the last stages of the operation. The lead sulphate is not entirely insoluble but can be made more so when alcohol is present. The acid should be added as long as a precipitate appears but a great excess is objectionable because of the large amount of ammonium hydrate which it would necessitate in the next step.

A very small quantity of copper gives the blue color with ammonium hydrate, which must be in excess to produce it. If the color is well marked the ferrocyanid test may be unnecessary.

It is necessary to confirm the bismuth by some other test than precipitation by ammonium hydrate, since if any of the lead had remained unprecipitated by sulphuric acid it also would form a white precipitate here. It does not, however, respond to the confirmatory test for bismuth.

[1] Although lead is classified with the metals of group I it will, if present, be found in part in group II.

The addition of potassium cyanid before testing for cadmium is to prevent the precipitation of the copper as a sulphid by hydrogen sulphid (76, 89). This being so much darker than the cadmium sulphid, the latter would probably escape detection.

Explanation of the Separation of the Metals of Group II, Division B.

Of the three precipitated sulphids only that of arsenic is soluble in ammonium carbonate, from which solution it is precipitated as As_2S_3 by acidifying. Either Gutzeit's or Reinsch's test will act with the suspended arsenous sulphid without its being filtered from the liquid.

The stannic sulphid with hydrochloric acid dissolves to $SnCl_4$, and the antimony sulphid to $SbCl_3$. The antimony compound is with difficulty attacked by the acid and for this reason it must be as far as possible free from water to avoid dilution of the acid. Boiling would weaken the latter by driving off the gaseous HCl. The chlorids of tin and antimony are both reduced to the metal by nascent hydrogen. This is produced by the action of an acid on zinc. If platinum is present the antimony is deposited upon it but the tin is not. Zinc almost always contains impurities which remain after it has dissolved. They are often black in color but float in the liquid while the tin is heavy and quickly settles. To confirm it the stannous chlorid is produced by the aid of concentrated hydrochloric acid and this is added to 2–3 cc. of mercuric chlorid, yielding white mercurous chlorid or gray metallic mercury. The reactions are as follows:

$$2HgCl_2 + SnCl_2 = 2HgCl + SnCl_4.$$
$$2HgCl + SnCl_2 = 2Hg + SnCl_4.$$

The fine coating of metallic antimony dissolves readily

in yellow ammonium sulphid to the sulph-antimonite and this is decomposed by the heat of evaporation to antimonous sulphid.

The sulphids of gold and platinum which do not dissolve in a single acid do so in aqua regia and can be precipitated from this by the ordinary reagents.

Practical Exercises in Group II.

1. Mix in a beaker 3–5 cc. each of solutions of mercury, lead, copper, bismuth and cadmium, and, after precipitating with hydrogen sulphid, separate the metals according to Table IV, division A.

2. In the same manner precipitate a mixture of the solutions of arsenic, antimony and tin with hydrogen sulphid and separate the mixed sulphids according to Table IV, division B.

3. For practice in separation of the group into its two divisions mix in the same way one or two from each division, *e. g.*, mercury, copper, arsenic and antimony. In making the selection it should be remembered that stannous solutions reduce mercuric compounds and that this and other chlorids precipitate lead in part, also that to keep bismuth, and sometimes antimony, in solution after dilution a considerable quantity of acid is required.

4. For further practice make analyses of unknown mixtures of the metals of group II furnished by the instructors.

Questions for Further Study on Group II.

What use is made in medicine of the fact that arsenous acid forms an insoluble compound with ferric or magnesium hydrate? How should the ferric hydrate be prepared for this purpose and what will be the most convenient materials? Soluble salts of what metals would be incompatible with solutions of arsenites and arsenates? Is the insolu-

bility of the arsenites and arsenates of the heavy metals sufficient to render these compounds non-poisonous? What classes of soluble compounds would be incompatible with solutions of metals of group II? Where and how is cupric hydrate used in testing for glucose? What is the difference between the red and the black mercuric sulphid? between yellow and red mercuric oxid? What is the pharmaceutical name of the yellow oxid and how is it prepared? What pharmaceutical names are applied to the mercuric ammonium chlorid? What medicinal substances have sufficient reducing powers to take the whole or a part of the chlorin from mercuric chlorid? With what class of medicinal compounds would a solution of mercuric chlorid in an excess of potassium iodid be incompatible? What compound of antimony most commonly causes acute poisoning? Could any of the above reagents be safely used to render it insoluble in the gastric juice? If so in what form or preparations could it be most conveniently obtained?

GROUP I.

Lead, Silver and Mercury (Mercurous Compounds).

They are precipitated from their solutions by hydrochloric acid. Their sulphids, carbonates, phosphates, oxids, hydrates, arsenates, arsenites, bromids, and iodids, as well as their chlorids, are insoluble in water, although lead chlorid is somewhat soluble.

Lead, Pb.

Lead is soluble in dilute nitric acid, more easily by the aid of heat, but is little affected by hydrochloric or sulphuric acids. Its soluble compounds are poisonous.

A great number of organic substances form insoluble compounds with lead acetate, which can consequently be used to remove them from solution.

For the reactions use a 1-per-cent. solution of $Pb(C_2H_3O_2)_2$.

154. Hydrogen sulphid or soluble sulphids give with lead solutions a black precipitate of lead sulphid, PbS, soluble in dilute nitric acid, sulphur being set free at the same time. If very strong nitric acid is used sulphuric acid is formed from the sulphur and this converts the lead into insoluble, white, lead sulphate, $PbSO_4$.

155. Sodium hydrate or potassium hydrate precipitates lead hydrate, $Pb(OH)_2$. This dissolves in an excess of the reagent with the formation of a plumbate of the alkali metal, Na_2PbO_2 or K_2PbO_2.

156. Ammonium hydrate precipitates a white basic salt which does not dissolve in an excess of the precipitant.

157. Sodium carbonate, or other soluble carbonates, precipitate white basic lead carbonate, $(PbCO_3)_2Pb(OH)_2$, soluble in acids, except sulphuric.

158. Hydrochloric acid or soluble chlorids in concentrated solutions of lead salts form a heavy white precipitate of lead chlorid, $PbCl_2$. This dissolves in hot water and on cooling, separates again in the form of needle-shaped crystals.

159. Sulphuric acid or soluble sulphates give a fine, heavy, white precipitate of lead sulphate, $PbSO_4$. From very dilute solutions it only appears after standing a long time. Free acids, except sulphuric, hinder its separation and alcohol hastens it. Lead sulphate dissolves in sodium hydrate.

160. Potassium chromate or dichromate precipitates yellow lead chromate, $PbCrO_4$, soluble in nitric acid or sodium hydrate.

161. Potassium iodid precipitates yellow lead iodid, PbI_2, from not too dilute solutions. This dissolves in boiling water from which it separates as the water cools.

162. Tannic acid precipitates yellowish lead tannate.

Mercurous Compounds, Hg′.

Use for the reactions a 1-per-cent. solution of $HgNO_3$.

163. Hydrogen sulphid or soluble sulphids produce with mercurous salts a black precipitate of mercuric sulphid mixed with mercury.

$$2HgNO_3 + H_2S = HgS + 2HNO_3 + Hg.$$

164. Sodium hydrate, potassium hydrate or calcium hydrate form a black precipitate of mercurous oxid, Hg_2O, insoluble in excess.

165. Ammonium hydrate precipitates a black mercurous ammonium salt.

$$2HgNO_3 + NH_4OH = Hg_2NH_2NO_3 + NH_4NO_3.$$

166. Hydrochloric acid or soluble chlorids precipitate fine, white, heavy mercurous chlorid, HgCl. This is soluble in aqua regia, being converted into mercuric chlorid, $HgCl_2$. It dissolves with much difficulty in nitric or hydrochloric acids singly. Ammonium hydrate changes it into black mercurous ammonium chlorid. Dry HgCl is slowly changed by sugar and some other organic substances into $HgCl_2$ and Hg.

167. Potassium iodid or soluble iodids precipitate greenish-yellow mercurous iodid, HgI.

168. Metallic copper and stannous chlorid give the same reactions as with the mercuric compounds. Other reducing agents act like stannous chlorid.

169. Nitric acid and other oxidizing agents change mercurous to mercuric compounds.

Silver, Ag.

Nitric acid readily dissolves silver but hydrochloric acid does not do so. Its soluble salts are poisonous.

Use for the reactions a 1-per-cent. solution of $AgNO_3$.

170. Hydrogen sulphid or soluble sulphids precipitate black silver sulphid, Ag_2S, which dissolves in boiling nitric acid.

171. Hydrochloric acid or soluble chlorids give a precipitate of heavy, curdy, white silver chlorid, AgCl. At the time of precipitation it is white, but by exposure to the light it gradually turns violet, then gray and finally black. In very dilute solutions it does not precipitate at first, the liquid becoming opalescent or milky. From this the precipitate slowly settles after it has stood for some time, or more rapidly by boiling. Silver chlorid is not soluble in nitric acid but dissolves readily in ammonium hydrate and is reprecipitated from this solution by acidifying with nitric acid.

172. Sodium hydrate, potassium hydrate or ammonium hydrate precipitate silver oxid, Ag_2O, which dissolves in an excess of the last but not of the two first named reagents.

173. Potassium chromate or dichromate forms a dark-red precipitate of silver chromate, Ag_2CrO_4.

174. Zinc, copper, mercury, tin or lead precipitate the metal.

175. Ferrous sulphate, $FeSO_4$, and other reducing agents separate the metal from its compounds.

Separation of the Metals of Group I.

Add hydrochloric acid to the solution. Silver and mercury (ous) are precipitated, with most of the lead, as chlorids. Filter and wash in cold water. Make a hole in the apex of the filter and with 10–15 cc. of water rinse the precipitate into a test-tube. Heat to boiling and filter while hot. The lead chlorid is dissolved. Test a portion of the filtrate after it is cold for this with dilute sulphuric acid. A fine white precipitate of lead sulphate is formed. From another portion with potassium dichromate precipitate yellow lead chromate.

After the precipitated chlorids of silver and mercury have been washed with hot water on the filter, pour over it 10 cc. of warm ammonium hydrate, receiving the filtrate in a clean test-tube. The silver chlorid dissolves. Mercurous chlorid is changed to a black solid which remains upon the filter.

Acidify the filtrate with nitric acid. The silver chlorid appears as a white precipitate or opalescence, soluble in ammonia and reprecipitated by nitric acid.

TABLE V.

OUTLINE OF SEPARATION OF THE METALS OF GROUP I.

To the solution of the mixed metals add HCl in excess. Filter and wash in cold water. The precipitate contains $PbCl_2$, AgCl and HgCl. All other groups present in the original solution pass into the filtrate. Boil the precipitate with water, filtering hot.

<table>
<tr><td rowspan="2">The filtrate contains $PbCl_2$. Test part with H_2SO_4; a fine white precipitate is lead sulphate.
Test part with $K_2Cr_2O_7$; a yellow precipitate is lead chromate.</td><td colspan="2">The insoluble residue contains AgCl and HgCl.
Dissolve the AgCl in warm NH_4OH.</td></tr>
<tr><td>Acidify the filtrate with nitric acid; a white precipitate is AgCl.</td><td>The mercury remains as black, insoluble NH_2Hg_2Cl.</td></tr>
</table>

Explanation of the Separation of the Metals of Group I.

This depends upon the solubility of the chlorids, lead chlorid dissolving in hot water but not easily in cold, and silver chlorid in ammonium hydrate, and not in hot water, the mercurous chlorid being insoluble in both.

The lead can be confirmed in the aqueous solution by any of its characteristic precipitants.

With ammonium hydrate silver chlorid forms ammonio-silver chlorid, $(AgCl)_2 3NH_3$, which is soluble. It is decomposed by acids, the silver chlorid separating again.

$$(AgCl)_2 3NH_3 + 3HNO_3 = 2AgCl + 3NH_4NO_3.$$

The detection of the mercurous chlorid is without diffi-

culty since it is the only one of the three which gives a dark color with ammonium hydrate.

Practical Exercise on Group I.

Mix in a test-tube 4–5 cc. each of solutions of silver, lead and mercurous salts and make the separation as given above.

Questions for Further Study on Group I.

Would the compounds of lead which are formed as precipitates be necessarily insoluble in the gastric juice? Are there any of the reagents which might be employed in cases of acute lead poisoning as antidotes? Would all of those which form insoluble compounds and which would thus prevent absorption, be suitable for such a purpose? What organic compounds commonly used medicinally would be incompatible with lead compounds? What is the common name of lead carbonate? In accordance with the above reactions what would be a safe and easily obtainable antidote for a poisonous dose of mercurous or silver nitrate? What is the pharmaceutical name of mercurous chlorid? How does it compare in its chemical properties and physiological action with mercuric chlorid? Would the chemical antidotes for mercurous chlorid necessarily precipitate mercuric chlorid? What is the danger of leaving dry mercurous chlorid for a long time mixed with organic substances? What is the pharmaceutical name of mercurous oxid and how is it prepared? Where is the turning dark of silver chlorid by light made use of practically?

The Separation of Metals into Groups.

The different metals can be precipitated in succession in groups from the original solution by using these group reagents in the following order:

1. Hydrochloric acid, which precipitates group I, silver, mercurous compounds and lead (in part).

2. Hydrogen sulphid, which precipitates group II, lead (remainder), mercuric compounds, copper, bismuth, cadmium, arsenic, antimony, tin, gold and platinum.

3. Ammonium sulphid (in the absence of phosphates, oxalates, borates, citrates and tartrates), which precipitates group III, cobalt, nickel, iron, manganese, chromium, zinc and aluminum.

4. Ammonium carbonate, which precipitates group IV, barium, strontium and calcium, but not magnesium.

Magnesium, sodium, potassium and ammonium are not precipitated by any of the above reagents.

The details of the separation are as follows:

To the cold solution which may contain all the metals add hydrochloric acid[1] as long as any precipitate forms. This contains group I. Separate the metals according to Table V. Filter, and to the filtrate add hydrogen sulphid until the liquid smells of this gas. Warm, stir to make the precipitate collect in large masses, then, if the precipitation is complete, filter and wash with warm water. The metals of group II, are on the filter, the remainder of the groups in the filtrate. Make the separation according to table IV. If the aqueous solution of hydrogen sulphid has been used to precipitate group II, and the filtrate is therefore of large volume, it may be concentrated to 40–50 cc. by boiling. It should then be made neutral or faintly alkaline by ammonium hydrate and, after the addition of ammonium chlorid, be precipitated by a slight excess of ammonium sulphid. Warm nearly to boiling, filter and wash. The precipitate contains the metals of group III. Separate

[1] In precipitating the different groups, when their presence or absence is uncertain, it is usually better to first test only a small portion of the solution with the group reagent, then, if a precipitate forms, to treat the whole in the same manner.

Table VI.

Outline of Analysis of Solution which may Contain Metals of all Groups, in Absence of Phosphates, Borates, Etc.

Pb, Ag, Hg′, Hg″, Cu, Bi, Cd, As, Sb, Sn, Au, Pt, Ni, Co, Fe, Mn, Cr, Zn, Al, Ba, Sr, Ca, Mg, K, Na, NH_4.

To the solution add HCl and filter.

- Precipitate = AgCl, HgCl, $PbCl_2$. Boil with water, filter and wash.
  - Filtrate = $PbCl_2$. Confirm Pb by H_2SO_4 or $K_2Cr_2O_7$.
  - Precipitate = AgCl, HgCl. Treat with warm NH_4OH.
    - Black residue = NH_2Hg_2Cl.
    - Solution = Ag. Acidify with HNO_3. White precipitate = AgCl.
- Filtrate = Hg″, Pb, Cu, Bi. Cd, As, Sb, Sn, Au, Pt, Ni, Co, Fe, Mn, Cr, Zn, Al, Ba, Sr, Ca, Mg, K, Na, NH_4. Add an excess of H_2S, warm, filter and wash.
  - Precipitate = HgS, PbS, CuS, Bi_2S_3, CdS, As_2S_3, Sb_2S_3, SnS or SnS_2, Au_2S_3, PtS_2. Digest in $(NH_4)_2S_x$ and filter.
    - Insoluble = HgS, PbS, CuS, Bi_2S_3, CdS. Wash and boil with HNO_3. Filter.
      - Precipitate = HgS. Dissolve in aqua regia and confirm by $SnCl_2$.
      - Filtrate = Pb, Cu, Bi, Cd. Add H_2SO_4. Filter.
        - Precipitate = $PbSO_4$. Dissolve in NaOH and confirm by H_2S.
        - Filtrate = Cu, Bi, Cd. Add NH_4OH in excess. Filter.
          - Precipitate = $Bi(OH)_3$. Confirm by NaOH + $SnCl_2$.
          - Filtrate = Cu, Cd.
            - In half confirm Cu by blue color, also by $K_4Fe(CN)_6$ + acid.
            - To half add KCN and precipitate Cd by H_2S.
    - Filtrate = As, Sb, Sn, Au, Pt. Acidify with HCl; filter; wash. Precipitate = As_2S_3, Sb_2S_3, SnS_2, Au_2S_3, PtS_2. Digest in $(NH_4)_2CO_3$, filter, wash.
      - Filtrate = As. Try Gutzeit's or Reinsch's tests.
      - Precipitate = Sb_2S_3, SnS_2, Au_2S_3, PtS_2. Warm with con. HCl. Filter.
        - Filtrate = $SnCl_4$, $SbCl_3$. Separate by Zn and Pt. Confirm Sn with $HgCl_2$ and Sb by conversion to Sb_2S_3 with $(NH_4)_2S_x$.
        - Insoluble = Au_2S_3, PtS_2. Dissolve in aqua regia
          - In half confirm Au by tin chlorids.
          - To half add NH_4Cl. Yellow precipitate = $(NH_4)_2PtCl_6$.
  - Filtrate[1] contains Ni, Co, Fe, Mn, Cr, Zn, Al, Ba, Sr, Ca, Mg, K, Na, NH_4. Add NH_4OH, NHCl and $(NH_4)_2S$. Warm, filter and wash.
    - Precipitate = NiS, CoS, FeS, MnS, ZnS, $Cr(OH)_3$, $Al(OH)_3$. Digest in cold dil. HCl. Filter and wash.
      - Insoluble = NiS, CoS. Test with borax bead or dissolve in aqua regia and separate with KNO_2 + CH_3CO_2H. (Page 53.)
      - Filtrate = Fe, Mn, Zn, Cr, Al. Expel H_2S, oxidize with Br water and add large excess of NaOH and boil. Filter and wash.
        - Precipitate = $Fe(OH)_3$, $Mn(OH)_2$, $Cr(OH)_3$.
          - Dissolve part in HCl and confirm Fe by $K_4Fe(CN)_6$.
          - Fuse remainder with Na_2CO_3 + KNO_3, Boil in water. Filter.
            - Mn = green mass. Insoluble.
            - Filtrate = Cr. Confirm with CH_3CO_2H + $Pb(CH_3CO_2)_2$.
        - Filtrate = Al, Zn. Acidify with HCl, add excess of NH_4OH and boil.
          - Precipitate = $Al(OH)_3$
          - Filtrate = Zn. Confirm by $(NH_4)_2S$ or $K_4Fe(CN)_6$ in acid solution.
    - Filtrate = Ba, Sr, Ca, Mg, K, Na, NH_4. Add $(NH_4)_2CO_3$ in excess, warm and filter.
      - Precipitate = $BaCO_3$, $SrCO_3$, $CaCO_3$. Dissolve in CH_3CO_2H and add $K_2Cr_2O_7$. Filter.
        - Precipitate = $BaCrO_4$. Confirm by flame.
        - Filtrate = Sr, Ca. Add H_2SO_4 and filter.
          - Precipitate = $SrSO_4$. Confirm by flame.
          - Filtrate = Ca. Add NH_4OH and $(NH_4)_2C_2O_4$. Precipitate = CaC_2O_4. Confirm by flame.
      - Filtrate contains Mg, K, Na, NH_4.
        - Test by flame with and without Co glass for K and Na.
        - Precipitate Mg with HNa_2PO_4.
        - Test for NH_4 in original solution by NaOH.

[1] If phosphates. oxalates, borates, etc., are present, this separation must be made by Table III.

them as in Table II or III. Boil the filtrate until the ammonium sulphid has been decomposed, as is shown by the disappearance of its odor, filtering out the sulphur if any has been set free. Precipitate group IV with ammonium carbonate, warming nearly to boiling to insure its complete separation. Filter and wash. Analyze the group by the use of Table I. If the filtrate is much diluted, evaporate to 20 or 30 cc. and apply the flame tests for sodium and potassium. Afterwards add to the solution sodium phosphate as a test for magnesium. Test the original substance for ammonium.

The Method of Analysis of Alloys Containing

Hg, Ag, Cu, Bi, Pb, Cd, Au, Pt, Sb, Sn, Ni, Co, Fe, Mn, Cr, Al, Zn.

Warm the fine alloy with equal parts of concentrated nitric acid and water under a hood until no gritty particles remain. Au, Pt, Sb and Sn are not dissolved; the others go into solution. Filter and wash.

Evaporate the filtrate to a small volume if much acid has been used and precipitate by an excess of H_2S, which forms insoluble sulphids of Hg, Ag, Cu, Bi, Pb and Cd. Stir until it settles, then filter and separate metals in the filtrate by Table II. Wash the precipitate well, then rinse it from the paper with about 10 cc. of nitric acid and separate the metals by Table IV, Division A.

If Au or Pt are contained in the first insoluble residue it will be dark in color. The compounds of Sb and Sn are white. Dissolve the moist precipitate in a little warm aqua regia and, after filtering, boil the solution a minute under the hood to expel the chlorin. Test half for Sn and Sb by metallic zinc and platinum (Table IV, Division B). Evaporate the excess of acid from the other half of the solution under a hood and dissolve in 3–4 cc.

of water. Test a part for Au by $SnCl_2$, which gives a purple color (purple of Cassius). To the rest add strong ammonium chlorid. Pt gives a yellow crystalline precipitate (151).

Practical Exercises on General Analysis.

For further drill the student should make analyses of as many unknown substances as possible, where all the groups must be sought for.

Questions for Further Study on the Metallic Compounds.

Which of the metals are incompatible with the alkaline hydrates because of their being precipitated? Does calcium hydrate have a similar action to that of the hydrates of the alkali metals? What hydrates have an alkaline reaction? What carbonates? What ones of the common pharmaceutical preparations have an alkaline reaction? Which groups of metals are precipitated by soluble carbonates? Of which ones are the carbonates soluble in water? What medicinal substances with an oxidizing action are the most commonly used in solution? What ones have a reducing action? What is meant by oxidizing and "reducing"? What compounds of the metals studied would be so far affected by the last-mentioned reagents as to cause an incompatibility? What classes of compounds would be incompatible with the metallic compounds of group I by rendering them insoluble? with group II? with group III? with group IV? with group V? What pharmaceutical preparations contain tannic acid? Does albumin form insoluble combinations with any other metallic compounds except mercuric salts? Are any other compounds decomposed by exposure to light with the exception of silver chlorid? What is the usual composition of precipitates produced by the action of a soluble hydrate

on a soluble metallic salt? by a soluble carbonate? Are there any exceptions to the usual rule? Knowing the composition of the reagent used, sulphid, phosphate, chromate, sulphate, etc., can we predict what will be the composition of the precipitate which it will form with a soluble compound of another metal?

CHAPTER II. ACIDS.

In testing for the presence of an acid we must distinguish between the acid in the free state and that which is combined as a salt (the hydrogen being wholly or in part replaced by a metal), as the reactions of one form often differ from those of the other. Free acids usually turn blue litmus red, but the same is true of many acid salts as well as of some normal salts of the heavy metals. The acids may be classified in a number of groups according to the similarity of their chemical action, but the actual separation of the acids from a complex mixture is not so simple a proceeding as that of the bases.

Sulphuric Acid, H_2SO_4, and Sulphates.

176. Pure sulphuric acid is a heavy, oily liquid (sp. gr. 1.85) which generates a large amount of heat when diluted with water, with which it forms a number of compounds. It dissolves many metals as sulphates.

177. The free acid chars most organic compounds when it is warmed with them by abstracting the elements of water and leaving the carbon. If the acid is dilute the charring only occurs after the water has been evaporated, leaving the concentrated acid. This can be shown upon paper or wood. Some organic compounds, including oxalic acid and its salts, also some of the alkaloids, are not thus blackened.

For the reactions of the salts a 1-per-cent. solution of any sulphate may be used.

178. Barium chlorid gives, in solutions of the free acid or its salts, a white, heavy, finely divided precipitate of

barium sulphate, $BaSO_4$, which is insoluble in acids and alkalies.

179. Lead acetate precipitates from solutions of sulphuric acid or sulphates heavy, white, finely divided, lead sulphate, $PbSO_4$. It is somewhat soluble in acids and, after washing, blackens when brought in contact with ammonium sulphid. It is not so sensitive a test as the preceding.

Sulphurous Acid, H_2SO_3, and Sulphites.

Sulphurous acid is produced when sulphurous oxid is dissolved in water. It is a colorless liquid with the odor of burning sulphur. It has an acid reaction and bleaches unstable coloring matters like those of the flowers. By exposure to the air it is oxidized readily to sulphuric acid. Its salts undergo the same chemical change. Both are consequently used as reducing agents. Only sulphites of the alkalies are soluble in water.

For the reactions use sodium sulphite.

180. Sulphites are decomposed by sulphuric acid with the evolution of SO_2, a heavy colorless gas which smells like burning sulphur. If a large test-tube is allowed to fill with it, after adding a little acid to a crystal of the sulphite, and the gas is then poured into another tube containing dilute potassium permanganate solution the latter is decolorized.

181. Barium chlorid gives with a neutral solution of a sulphite a white precipitate of barium sulphite, $BaSO_3$, which dissolves in hydrochloric or nitric acids.

182. Silver nitrate precipitates from solutions of sulphites white silver sulphite, $AgSO_3$, which upon warming turns black with a formation of metallic silver and sulphuric acid.

$$Ag_2SO_3 + H_2O = Ag_2 + H_2SO_4.$$

183. Oxidizing agents like nitric acid, bromin or chlorin water, and many others convert sulphites into sulphates

which then give with barium chlorid a precipitate that is insoluble in acids.

184. Sulphurous acid or sulphites evolve hydrogen sulphid when warmed with dilute sulphuric acid and zinc. This gas turns lead acetate paper brown or black and can be identified by its odor likewise.

Carbonic Acid, H_2CO_3, and Carbonates.

Carbon dioxid (carbonic anhydrid) when dissolved in water forms carbonic acid, H_2CO_3, which reddens litmus paper. It exists only in salts and in solution, which latter is readily decomposed by heating, the carbon dioxid being expelled. Of the carbonates only those of the alkalies are very soluble in water and these when dissolved have a strong alkaline reaction.

For the reactions sodium carbonate may be used.

185. Carbonates are decomposed by almost all free acids, usually without heating, although this is sometimes necessary. The gas which escapes with effervescence is carbon dioxid. It can be identified by its rendering lime-water milky. It is a colorless, odorless gas, so much heavier than air that it can be poured from the test-tube where it is evolved into another containing two or three cc. of lime-water. If the tube is now shaken so as to mix the two, the liquid is turned white — a characteristic reaction. It may also be shown by holding a drop of the lime-water down in the tube of gas on the end of a glass rod, being careful not to let the drop run off by touching the side of the tube. The precipitate dissolves in HCl.

186. The acid carbonates or bicarbonates, like $NaHCO_3$, are less stable than the normal carbonates, like Na_2CO_3 or $CaCO_3$, and are decomposed when heated in water before this reaches its boiling point, half the carbon dioxid escaping. The normal carbonates are not thus decomposed.

Soluble normal carbonates will turn yellow turmeric paper reddish-brown, while the acid carbonates do not, if they contain none of the normal compound, although this is very commonly present.

187. Barium chlorid, with carbonates soluble in water, gives a white precipitate of barium carbonate, $BaCO_3$. In very dilute solutions it appears only after heating to boiling. It is soluble in most acids except sulphuric. No precipitate is produced in barium chlorid with the free carbonic acid.

Oxalic Acid, $H_2C_2O_4$, and Oxalates.

The acid is a white solid, readily soluble in water and crystallizing from its solution with two molecules of water of crystallization. It has an intensely sour taste and is strongly acid to litmus.

188. Pure oxalic acid volatilizes without leaving a residue when heated on a platinum foil, giving irritating fumes. Oxalates of the non-volatile bases treated in the same manner are partly vaporized but leave a residue behind, the carbonate of the base.

For reactions of the oxalates ammonium oxalate may be employed.

189. When heated nearly to boiling with concentrated sulphuric acid the solid oxalic acid or an oxalate is decomposed, yielding carbon dioxid, carbon monoxid and water. The former can be identified by the turbidity which it produces in lime-water and the latter by the bright blue flame when it is ignited. Oxalic acid is not blackened by strong sulphuric acid.

190. Barium chlorid precipitates from neutral solutions of the oxalates white, pulverulent, barium oxalate, BaC_2O_4. It is insoluble in acetic acid. It dissolves in hydrochloric acid and is reprecipitated from this by ammonia. Calcium salts give a similar result, even in very dilute solutions.

191. Potassium permanganate solution is quickly decolorized when warmed with oxalic acid or one of its salts, after acidifying with sulphuric acid. This is because of the strong reducing power of the acid. For the same reason an acidified solution of potassium dichromate is likewise reduced by it to a green chromic salt.

Chromic Acid, H_2CrO_4, and Chromates.

Chromic anhydrid, CrO_3, when dissolved in water forms chromic acid, which only exists in solution. The acid and the chromates are all colored red or yellow. The normal chromates like K_2CrO_4 which contain two univalent metallic atoms to each acid radical, are yellow, but upon acidifying they become reddish by the abstraction of a part of the base and the formation of bichromates, also called dichromates, like $K_2Cr_2O_7$. Chromic anhydrid and chromates act as oxidizing agents, being at the same time changed to chromic salts, if free mineral acids are present.

For the reactions use a 2-per-cent. solution of potassium dichromate.

192. Barium chlorid precipitates from solutions of chromates yellow barium chromate, $BaCrO_4$, insoluble in acetic but soluble in hydrochloric acid.

193. Lead acetate precipitates lemon-yellow lead chromate, $PbCrO_4$, soluble with difficulty in nitric acid, readily soluble in sodium hydrate.

194. Hydrogen sulphid slowly changes an acidified solution of a chromate to brown, then green, chromic salt, without precipitation.

195. Ammonium sulphid on warming precipitates from a solution of a chromate bluish-green chromic hydrate, $Cr(OH)_3$.

196. Concentrated hydrochloric acid evolves chlorin when warmed with a chromate, the chlorid of the metal

being produced at the same time. The color of the solution is changed from yellow to green.

197. Alcohol or oxalic acid is oxidized by a solution of potassium dichromate acidified strongly with sulphuric acid, the color of the dichromate being changed to green.

Boric Acid (Boracic Acid), H_3BO_4, and Borates.

The free acid is a white, crystalline solid, soluble in water. It reddens litmus paper and turns to a reddish-brown paper which has been colored yellow by a solution of turmeric. It is somewhat volatile with boiling water or alcohol and when the latter is ignited it imparts a green border to the flame. The borates of metals except those of the alkalies are insoluble in water but soluble in most acids.

For the reactions a 2-per-cent. solution of borax may be used.

198. Barium chlorid precipitates, except in dilute solutions, white barium borate.

199. A few grains of the solid moistened with a few drops of concentrated sulphuric acid in a porcelain dish will give a green-bordered flame when mixed with 2–3 cc. of alcohol and the latter is set on fire. The free acid does the same without the addition of sulphuric acid (compare with 82).

200. Slightly acidify the solution of a borate with hydrochloric acid, dip into this a piece of turmeric paper and dry the latter at a gentle heat. It is turned reddish-brown. Moistening this with an alkali turns it bluish or greenish-black.

201. From a hot, concentrated solution of a borate hydrochloric acid precipitates free boric acid which separates in white crystalline scales.

Orthophosphoric Acid, H_3PO_4, and Orthophosphates.

This is the most common acid of phosphorus and is the one which is meant when phosphoric acid is spoken of without any distinguishing prefix. Although it can be obtained in the crystalline form it is very deliquescent, so that it usually appears as a liquid, thick and syrupy when concentrated. It has a strong acid reaction and taste.

For testing use a 2 per-cent. solution of sodium phosphate, Na_2HPO_4.

202. Barium chlorid precipitates from solutions of phosphates white barium phosphate, $BaHPO_4$, soluble in hydrochloric acid. It does not produce this with solutions of the free acid.

203. Magnesia mixture (the clear solution produced by adding to magnesium sulphate ammonium chlorid, then making it alkaline with ammonium hydrate) precipitates from solutions of phosphates white ammonium magnesium phosphate, NH_4MgPO_4. Under the microscope it is seen to be in the form of snowflake-shaped crystals. The compound is soluble in acids. In dilute solutions the precipitation is slow and is favored by shaking or stirring.

204. If 0.5 cc. of a solution of phosphoric acid or its salts is added to 5 cc. of ammonium molybdate in nitric acid and the mixture slightly warmed a yellow precipitate of ammonium phosphomolybdate $(NH_4)_3PO_4(MoO_3)_{10}$, $2H_2O$ forms slowly. It is easily soluble in ammonium hydrate and its formation is hindered by the presence of chlorids and of some organic compounds.

205. From solutions of phosphates, containing no free acid, ferric chlorid precipitates yellowish-white, gelatinous ferric phosphate. If a little mineral acid is present it can be removed by the addition of a few crystals of sodium acetate. An excess of ferric chlorid should then be avoided as it produces reddish ferric acetate.

206. A solution of egg-albumin is not precipitated by orthophosphoric acid nor by solutions of orthophosphates acidified with acetic acid.

Metaphosphoric Acid, HPO_3, and Metaphosphates.

The free acid is a transparent, ice-like solid, readily soluble in water. Boiling in water changes it into orthophosphoric acid. The solution when mixed with zinc oxid yields a plastic mass which hardens on standing.

A 2-per-cent. solution of sodium metaphosphate can be used for testing.

207. Barium chlorid precipitates from neutral solutions barium metaphosphate, $Ba(PO_3)_2$, soluble in hydrochloric acid.

208. Magnesia mixture (203) with the metaphosphates, gives no precipitate that is insoluble in ammonium chlorid.

209. Ammonium molybdate also fails to form a precipitate.

210. Free metaphosphoric acid, or solutions of metaphosphates when acidified with acetic acid, will precipitate a solution of egg-albumin. (Difference from orthophosphoric acid.)

Hypophosphorous Acid, HPH_2O_2, and Hypophosphites.

The hypophosphites are nearly all soluble in water. By heating the dry salts they are decomposed into phosphates and hydrogen phosphid, PH_3, a combustible gas which before burning has the odor of decaying fish.

$$2NaPH_2O_2 = H_3P + Na_2HPO_4.$$

Oxidizing agents convert them into phosphates.

Use for the reactions a 2-per-cent. solution of $NaPH_2O_2$.

211. Silver nitrate precipitates, first, white silver hypophosphite, $AgPH_2O_2$, from which black metallic silver soon separates, the latter change being hastened by warming.

$$2NaPH_2O_2 + 2AgNO_3 = Ag_2 + 2NaH_2PO_4 + N_2O_2.$$

212. Mercuric chlorid slowly forms white insoluble mercurous chlorid, HgCl, more rapidly on heating.

$$NaPH_2O_2 + 4HgCl_2 + 2H_2O = 4HgCl + NaH_2PO_4 + 4HCl.$$

Long heating changes the color of the chlorid to gray from the separation of metallic mercury.

213. Hypophosphites readily decolorize a solution of $KMnO_4$.

214. Barium chlorid or lead acetate gives no precipitate.

215. When warmed with concentrated sulphuric acid the hypophosphites cause an evolution of sulphurous oxid.

Thiosulphuric Acid, $H_2S_2O_3$, and Thiosulphates ("Hyposulphites").

The acid does not exist free. Its salts are mostly soluble and act as reducing agents.

Sodium thiosulphate can be used for the reactions.

216. Silver nitrate produces a white precipitate of silver thiosulphate, $Ag_2S_2O_3$. It dissolves in an excess of the thiosulphate and is therefore not readily precipitated from concentrated solutions of the latter salt. When heated it turns black, silver sulphid being precipitated.

217. Barium chlorid precipitates white barium thiosulphate, BaS_2O_3, which is somewhat soluble in water.

218. Solutions of thiosulphates are decomposed by the mineral acids with an evolution of sulphurous oxid, sulphur being at the same time precipitated.

219. An acidified solution of potassium permanganate is immediately decolorized by a thiosulphate.

Hydrosulphuric Acid (Hydrogen Sulphid), H_2S, and Sulphids.

Hydrosulphuric acid is a colorless gas with the odor of decaying eggs. It dissolves in about one-third of its

volume of water at ordinary temperatures and this solution reddens litmus paper. By the addition of alkaline hydrates to this sulphids are formed.

$$2NH_4OH + H_2S = (NH_4)_2S + 2H_2O.$$

Of its salts only those of the alkalies and alkaline earths are soluble in water. These, together with the sulphids of iron, manganese and zinc evolve hydrogen sulphid when treated with sulphuric acid. The sulphids of some of the heavy metals like copper, mercury and lead give sulphurous oxid instead. Solutions of the sulphids dissolve sulphur with the formation of the polysulphids—

$$(NH_4)_2S + S = (NH_4)_2S_2, \text{ etc.}$$

For the reactions a 1-per-cent. solution of Na_2S can be used.

220. Lead acetate or silver nitrate with the free acid or solutions of soluble sulphids form black precipitates of lead sulphid, PbS, or silver sulphid, Ag_2S.

221. Soluble sulphids when acidified with hydrochloric or sulphuric acid give hydrogen sulphid, identified by its odor or by its turning brown or black a paper previously dipped in a solution of lead acetate.

222. Polysulphids give the same when acidified, and also precipitate sulphur, very fine and nearly white.

223. Mercuric sulphid, lead sulphid, and some of the other insoluble sulphids yield no hydrogen sulphid when warmed with hydrochloric acid, but do so if at the same time a fragment of zinc is present.

Hydroferrocyanic Acid, $H_4Fe(CN)_6$, and Ferrocyanids.

Use for the reaction a 1-per-cent. solution of $K_4Fe(CN)_6$.

224. Ferric chlorid forms a deep-blue precipitate of ferric ferrocyanid (62).

225. Copper sulphate produces a reddish-brown precipitate of copper ferrocyanid (80).

226. Ferrocyanids heated with concentrated sulphuric acid liberate carbon monoxid; with dilute sulphuric acid hydrocyanic acid, HCN, is set free. (Danger!)

Hydroferricyanic Acid, $H_3Fe(CN)_6$, and Ferricyanids.

Use a 1-per-cent. solution of $K_3Fe(CN)_6$ for the reactions.

227. Ferric chlorid with soluble ferricyanids gives no precipitate but turns the liquid brown (63).

228. Ferrous salts produce a deep-blue precipitate with solutions of ferricyanids (55).

Sulphocyanic Acid, HSCN, and Sulphocyanates.

A 1-per-cent. solution of KSCN may be used for testing.

229. Ferric chlorid forms a deep-red liquid, but no precipitate, with sulphocyanates (64). The color disappears upon the addition of mercuric chlorid.

Hypochlorous Acid, HClO, and Hypochlorites.

A solution of NaClO may be used for the reactions.

230. Acidifying hypochlorites with hydrochloric acid sets chlorin free. This can be recognized, if sufficient is present, by its color, odor and bleaching moist litmus paper.

231. Soluble hypochlorites bleach indigo solution,—more rapidly after acidifying.

232. Hypochlorites do not bleach acid solutions of potassium permanganate.

233. Lead acetate forms, first, a white precipitate which gradually becomes reddish, then brown from the formation of the dioxid, PbO_2.

$$9NaClO + Pb(C_2H_3O_2)_2 = PbO_2 + 9NaCl + 4CO_2 + 3H_2O.$$

Nitrous Acid, HNO_2, and Nitrites.

$NaNO_2$ can be used for the reactions.

234. By acidifying solutions of nitrites, nitrous acid is set free. It is extremely unstable and is not used in the

free state. From the solid salts or strong solutions a brown mixture of the oxids of nitrogen appears when acid is added.

$$2NaNO_2 + H_2SO_4 = Na_2SO_4 + H_2O + NO + NO_2.$$

235. The free acid or acidified solutions of its salts decolorize indigo solution upon heating.

236. Nitrites when acidified will decolorize potassium permanganate.

237. From a few drops of potassium iodid solution acidified with hydrochloric acid, nitrites set iodin free. Starch solution then gives a blue color with the iodin.

$$2NaNO_2 + 2KI + 4HCl = 2KCl + 2NaCl + N_2O_2 + 2H_2O + I_2.$$

Ferric salts and a few other compounds, notably iodic acid, also decompose potassium iodid.

Other reactions for minute amounts of nitrites are given under Water Analysis.

Hydrochloric Acid, HCl, and Chlorids.

Hydrochloric acid is a colorless gas with a suffocating odor and very soluble in water, in which form it is commonly used. Most of its salts are also soluble in water.

238. Addition of concentrated sulphuric acid to the dry salts produces an evolution of hydrochloric acid gas. This has a strong odor and acid reaction. If manganese dioxid is also present chlorin is set free, recognizable by its color and odor.

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

$$4HCl + MnO_2 = MnCl_2 + 2H_2O + Cl_2.$$

A 1-per-cent. solution of NaCl will give the other reactions.

239. Silver nitrate precipitates white, curdy silver chlorid, AgCl, which, in very dilute solutions, remains for a long

time in suspension. It is insoluble in nitric acid but easily dissolves in ammonium hydrate and can be reprecipitated from this solution by nitric acid. By exposure to sunlight the white compound turns violet, then nearly black.

240. Lead acetate forms a white precipitate of lead chlorid, $PbCl_2$, which dissolves in boiling water and, when this cools, separates again as white prismatic crystals.

Hydrobromic Acid, HBr, and Bromids.

The free acid is similar to hydrochloric in physical as well as chemical properties. For the reactions use potassium bromid.

241. From a crystal of a dry bromid concentrated sulphuric acid liberates bromin upon warming. This is seen as a reddish-yellow gas, most plainly by looking down into the test-tube. The addition of a little manganese dioxid increases the evolution of the gas. Nitric acid also sets free bromin from most bromids when it is heated, if in a solution coloring the liquid yellow.

242. Silver nitrate precipitates from solutions of bromids, even when dilute, yellowish-white, curdy silver bromid, AgBr. It does not dissolve in nitric acid and is soluble with some difficulty in ammonium hydrate.

Hydriodic Acid, HI, and Iodids.

The acid resembles, physically and chemically, hydrochloric and hydrobromic acids.

243. A small crystal of the dry salt is decomposed by heating with concentrated sulphuric acid, iodin being evolved and volatilized as a deep purple vapor. Yellow nitric acid produces the same effect as sulphuric when boiled with the salt even in comparatively dilute solutions. A very slight amount of this vapor turns to a deep bluish-black a paper moistened or sized with starch solution.

A 1-per-cent. solution of potassium iodid may be used for the wet reactions.

244. From a solution of an iodid, bromin water or chlorin water sets free iodin which gives a dark blue color to a solution of starch. An excess of the chlorin water destroys the color. Iodids alone do not color the starch.

245. Silver nitrate precipitates from solutions of iodids yellowish silver iodid, AgI, insoluble in nitric acid and nearly insoluble in ammonium hydrate.

Hydrocyanic Acid, HCN, and Cyanids.

The free acid is a colorless liquid, very volatile, with the odor of bitter almonds, and extremely poisonous. The gas burns with a violet flame. The cyanids of the alkalies and alkaline earths are soluble in water. Weak acids, including carbonic, liberate the acid from these but not from all cyanids. The insoluble cyanids of the heavy metals form soluble cyanids with those of the alkalies, consequently potassium cyanid dissolves most of the former class.

Use for the reactions a 1-per-cent. solution of KCN.

246. Silver nitrate forms a white precipitate of silver cyanid, AgCN, which is insoluble in nitric acid and but slightly so in ammonium hydrate but is soluble in KCN.

247. A few drops of ferrous sulphate in a solution of a cyanid is converted by warming, after making alkaline with sodium hydrate, into the ferrocyanid.

$$6KCN + FeSO_4 = K_4Fe(CN)_6 + K_2SO_4.$$

Upon acidifying with hydrochloric acid and adding a few drops of ferric chlorid (the latter is unnecessary if the ferrous sulphate contained any ferric salt) a deep blue color appears (62).

248. Acidification of solutions of cyanids evolves the free acid, recognizable from its odor. From its poisonous

nature it is dangerous to inhale. Concentrated sulphuric acid decomposes the insoluble cyanids in the same manner.

Nitric Acid, HNO_3, and Nitrates.

Almost all nitrates are soluble in water and all are decomposed with the evolution of oxygen when heated to a red heat.

249. The free acid is a colorless liquid, very strongly corrosive. It colors proteid compounds, like horn, feathers, quill toothpicks, etc., a bright yellow.

KNO_3 can be used for the reactions.

250. At high temperatures nitrates give up their oxygen to oxidizable substances like charcoal, causing deflagration. A few crystals dropped on a piece of red-hot charcoal will illustrate this.

251. In a narrow test-tube place 3–4 cc. of a solution of a nitrate, then holding it in a slanting position slowly pour in as much concentrated sulphuric acid. The two liquids do not mix. If much heat is generated cool it by holding the tube in running water; then add a few drops of a strong solution of ferrous sulphate. A brownish-purple ring forms at the junction of the liquids. With minute amounts of the acid this appears only slowly.

252. Nitric acid heated with metallic copper (or nitrates with this and in addition a few drops of concentrated sulphuric acid) liberates nitric oxid which produces a brownish gas in the upper part of the test-tube.

253. Nitric acid or a solution of a nitrate acidified with hydrochloric acid will decolorize indigo on warming. It should, however, be remembered that chlorin and some other oxidizing agent will do the same.

Other more sensitive tests for minute amounts of nitric acid are given under the subject of water analysis.

Chloric Acid, $HClO_3$, and Chlorates.

The free acid is not used. Its salts are strong oxidizing agents yielding oxygen more easily than the nitrates. They deflagrate on red-hot charcoal.

Use $KClO_3$ for the reactions.

254. Chlorates give no precipitate with silver nitrate, but when heated on platinum foil they lose all their oxygen, becoming converted to chlorids which then react with the above reagent (239).

255. Concentrated sulphuric acid warmed with a fragment of a dry chlorate liberates chlorin tetroxid, Cl_2O_4, a greenish-yellow explosive gas. It is dangerous to use large amounts of substance or to heat rapidly.

256. Hydrochloric acid will evolve chlorin when warmed with a chlorate, as is proven by the characteristic color and odor.

$$KClO_3 + 6HCl = KCl + 3H_2O + 6Cl.$$

Some oxids of chlorin may also be formed. The liquid destroys the blue color of an indigo solution.

Acetic Acid, CH_3CO_2H, and Acetates.

The free acid is a colorless liquid with a sharp odor and sour taste. It is easily volatile and its vapor is combustible. Most of its salts are decomposed by heating to a red heat, the residue being black. But few acetates are insoluble.

A 2-per-cent. solution of CH_3CO_2Na may be used for the reactions.

257. A dry acetate heated with dilute sulphuric acid, or a solution of an acetate heated with concentrated acid evolves acetic acid which distils with the characteristic odor.

258. If in the above test a cubic centimeter of alcohol is added before heating, acetic ether (ethyl acetate) is produced and this can be identified by its agreeable, fruity odor.

259. Ferric chlorid imparts a deep red color to solutions of neutral acetates or to acetic acid when the mixture is nearly neutralized by ammonium hydrate. Boiling this precipitates the iron. Acidifying with hydrochloric acid turns it yellow (64).

Tartaric Acid, $C_2H_4O_2(CO_2H)_2$, and Tartrates.

Tartaric acid is a white crystalline solid, with an acid taste, easily soluble in water.

Tartrates prevent the precipitation by the alkaline hydrates of copper, iron and some other bases ordinarily precipitated thus.

$C_2H_4O_2(CO_2)_2KNa$ may be used for the reactions.

260. Dry tartaric acid or the tartrates are charred when warmed with concentrated sulphuric acid. Both it and its salts are decomposed when highly heated dry, the residue being black and the decomposition attended by an odor similar to that of burnt sugar.

261. Barium chlorid precipitates from solutions of tartrates white barium tartrate, $BaC_4H_4O_6$, soluble in ammonium salts or hydrochloric acid.

262. From solutions of tartrates silver nitrate precipitates white silver tartrate, $Ag_2C_4H_4O_6$. If this is boiled black metallic silver separates. By dropping into the white precipitate before boiling enough ammonium hydrate to dissolve it, then slowly warming it in a test-tube that has been thoroughly cleaned with sodium hydrate and water, the silver deposits as a mirror on the tube The heating may be accomplished by setting the tube in a beaker of hot water.

Citric Acid, $C_3H_5O(CO_2H)_3$, and Citrates.

The free acid is a crystalline, colorless solid containing one molecule of water of crystallization. It is efflorescent, readily soluble in water and has an acid taste. When

heated it melts, and afterwards decomposes with blackening and the production of an odor, which, however, is different from that of tartaric acid. In the presence of citrates the alkaline hydrates fail to precipitate iron and many of the other bases.

$K_3C_6H_5O_7$ may be used for the reactions.

263. Citric acid and its salts are decomposed by hot concentrated sulphuric acid with carbonization.

264. Barium chlorid forms a white precipitate of barium citrate, $Ba_3(C_6H_5O_7)_2$, in strong solutions. In dilute solutions it may not appear until after heating.

265. Silver nitrate precipitates white silver citrate, $Ag_3C_6H_5O_7$, but this does not reduce to the metallic silver when it is warmed.

The Identification of the Acids when Only One is Present.

As a preliminary test warm a piece of the powdered dry substance as large as a pea in a test-tube with two cc. of concentrated sulphuric acid. Avoid heating to the boiling point of the sulphuric acid. Notice whether there is an evolution of gas as shown by the formation of bubbles in the hot liquid.

A. A Colorless Gas is Evolved.

Chlorids give HCl (odor).

Cyanids give HCN (odor). (Danger !)

Carbonates give CO_2.

Nitrates give HNO_3 (odor).

Sulphites give SO_2 (odor).

Hypophosphites give SO_2 (odor).

Sulphids give H_2S (odor), although some sulphids of the heavy metals evolve SO_2 from hot sulphuric acid.

Ferrocyanids, ferricyanids and sulphocyanates give a mixture of gases, sometimes HCN. (Danger !)

Thiosulphates give SO_2 (odor).

Acetates give acetic acid (odor).

Oxalates give CO and CO_2.

Some salts of organic acids liberate colorless gases.

B. A Colored Gas is Evolved.

Iodids give HI and iodin (violet).

Bromids give HBr and bromin (reddish-brown).

Nitrates give HNO_3 with oxids of nitrogen (brown or yellowish-brown).

Nitrites give oxids of nitrogen (yellowish-brown).

Chlorates give greenish-yellow oxids of chlorin (explosive).

Hypochlorites give chlorin (suffocating odor).

C. No Gas is Evolved and No Blackening is Seen.

Sulphates.

Phosphates.

Borates.

Chromates.

Arsenates.

Arsenites.

D. Many salts of organic acids as well as some organic compounds which are not salts are blackened by the strong sulphuric acid and in some cases colorless gases are set free.

If the preliminary test with sulphuric acid indicates the acid present confirm it by the identification of its group, then by the reactions given under the acid.

In case the preliminary test does not give definite results dissolve the substance in water if possible, if not, in a very small amount of nitric acid. Determine the class to which the acid belongs, using separate portions of the solution for each test. To identify the acid after this has been done compare its reactions with those of all the acids of the class.

Although it is possible to group the acids in accordance with their similarities, the groups cannot be separated from each other and be afterwards resolved into their components as easily as can the metals. Such an analysis is often accompanied with many difficulties. The following classification will aid in the identification of the acid radical of salts when only one is present or, if several, provided they are not of the same group.

GROUP I.

Precipitated by $BaCl_2$[1] in solution acidified by HNO_3.

Sulphuric acid, H_2SO_4; (sulphates).

GROUP II.

Carefully neutralize the solution with NH_4OH if it is acid. If the base is precipitated filter it out[2] and test the filtrate for the acid with $BaCl_2$.[1] The acids of this group give a white or colored precipitate, soluble in HCl or HNO_3. They are of two classes:

Class 1.—The solid substance evolves a gas with hot concentrated H_2SO_4.

Carbonic acid, H_2CO_3; (carbonates).[3]

Sulphurous acid, H_2SO_3; (sulphites).[3]

Oxalic acid, $H_2C_2O_4$; (oxalates).

Citric acid, $C_6H_8O_7$; (citrates).

[1] If the base is one which will be precipitated by a chlorid (lead, silver or mercurous) $Ba(NO_3)_2$ must be used instead of $BaCl_2$.

[2] Salts of acids in group II., except where the base is an alkali metal, are mostly insoluble in neutral or alkaline liquids. Both base and acid will therefore be precipitated when the solution is neutralized.

[3] Carbonates and sulphites which are insoluble in water cannot be dissolved in acid and the solution is tested with a barium solution. Why? (180, 185.)

Class 2. — The solid does not evolve a gas with sulphuric acid.

Chromic acid, H_2CrO_4; (chromates).

Phosphoric acid, H_3PO_4; (phosphates).

Arsenic acid, H_3AsO_4; (arsenates).

Boric acid, H_2BO_3; (borates).

GROUP III.

The acids of this group give precipitates with $AgNO_3$ in the presence of HNO_3. It contains four classes.

Class 1. — The precipitate with $AgNO_3$ turns black at once or on warming. Much HNO_3 prevents this.

Thiosulphuric acid, $H_2S_2O_3$; (thiosulphates, sometimes called "hyposulphites").[1]

Hydrosulphuric acid, H_2S; (sulphids, including polysulphids).

Hypophosphorous acid, HPH_2O_2; (hypophosphites).

Class 2. — These acids give a red or blue color with ferrous or ferric salts.

Sulphocyanic acid, HSCN; (sulphocyanates or "sulphocyanids").

Hydroferrocyanic acid, $H_4Fe(CN)_6$; (ferrocyanids).

Hydroferricyanic acid, $H_3Fe(CN)_6$; (ferricyanids).

Class 3. — These acids bleach indigo solution at once or on warming.

Hypochlorous acid, HClO; (hypochlorites).

Nitrous acid, HNO; (nitrites).

Class 4. — Belong to none of the first three classes.

Hydrochloric acid, HCl; (chlorids).

Hydrobromic acid, HBr; (bromids).

Hydriodic acid, HI; (iodids).

Hydrocyanic acid, HCN; (cyanids).

[1] Since silver thiosulphate is soluble in an excess of thiosulphates it may not appear if too strong a solution of the thiosulphate is used.

GROUP IV.

Give no precipitates with barium salts or with silver nitrate in the presence of nitric acid.

Nitric acid, NHO_3; (nitrates).

Chloric acid, $HClO_3$; (chlorates).

Acetic acid, CH_3CO_2H; (acetates).

Tartaric acid, $C_2H_4O_2(CO_2H)_2$; (tartrates).

Practical Exercises on the Acids and Their Salts.

Determine the composition of the unknown salts furnished by the instructors looking up their physical and chemical properties, their manufacture, their uses, etc. If a negative result is obtained in the examination for a base the substance may be an uncombined acid. If the examination fails to show any acid it may be an oxid or a hydrate. The hydrates of the alkalies and alkaline earths form alkaline solutions in water; the others are insoluble. All but the hydrates of the alkalies are decomposed to water and an oxid when heated in a dry tube. The oxids do not yield water on heating. All are insoluble in water except those of the alkalies and alkaline earths which dissolve as hydrates. The peroxids and a few others, as those of mercury, give off oxygen when heated.

Questions for Further Study on the Reactions of the Acids.

Where is any practical use made of the affinity of strong sulphuric acid for water? In diluting the acid which is the safer, to add the acid to the water or to add the water to the acid? Will the strong acid char such an organic compound as alcohol by removing the elements of water? What gas is evolved when a metal dissolves in sulphuric acid? Does it make any difference whether the acid is concentrated or dilute? Is it a compound of sulphuric acid

which is precipitated from the aromatic acid when it is diluted with water? The salts of what metals are precipitated by sulphates? Why is sulphuric acid selected for making the preliminary test? Why is it not in all cases the weaker acid which is thus liberated?

Why do the sulphites so often contain sulphates? What effect do sulphites have on solutions of salts of which there are two classes, the *ous* and *ic*, like the mercurous and mercuric, ferrous and ferric, arsenous and arsenic? Will other acids than sulphuric set free the sulphurous acid from its salts? What is the chemical action of sulphurous acid upon potassium permanganate or the chromates? What is the chemical action by which hydrogen sulphid can be produced from sulphurous acid and its salts, and what is the active agent?

With solutions of what metals are soluble carbonates incompatible because of the precipitation of the former? Are carbonates ever decomposed by salts which have an acid reaction or only by free acids? What compound is formed when carbon dioxid acts upon lime-water? What would be the effect of a large excess of the gas? How are the bicarbonates produced and why are they so called? What application is made of the easy decomposition of the bicarbonates?

What is the physiological action of oxalic acid or the soluble oxalates? Are many of the other organic acids volatilized by heat without discoloration? What is meant by "reducing power"?

What would be the objection to triturating a dichromate with tannic acid or sugar? Why does a solution of a dichromate turn from red to yellow when it is made alkaline? For what is chromic anhydrid used? What is the difference between a salt of chromic acid and a chromium salt?

How are the two phosphoric acids made? Will soluble phosphates be incompatible with the salts of other metals besides iron, magnesium and calcium? The phosphates of which metals are soluble in water? Will acids and alkalies increase or decrease the solubility of phosphates? What is the commercial name of metaphosphoric acid? Which phosphoric acid is official in the U. S. P.? How much of the hydrogen of orthophosphoric acid can be replaced by metals to form salts? How much in hypophosphorous acid? How do salts of phosphoric acid formed by replacing varying amounts of hydrogen differ from each other? What use is made of the zinc compounds of metaphosphoric acid? What property of the hypophosphites accounts for their decolorizing a permanganate solution? What is the chemical change which occurs when hypochlorites decolorize indigo solution? What is the change in nitrites when they decolorize a permanganate solution? Is their chemical action always of this kind when mixed with other compounds? Is the chemical nature of the organic nitrites used medicinally the same as of the inorganic salts? Is the chemical activity of nitrites different in acidified solutions from that of neutral or alkaline solutions? With what class of substances do nitrites often form colored compounds?

What metallic salts of the halogens are insoluble in cold water? What is the effect of strong oxidizing agents on hydrochloric acid? How do the compounds of chlorin, bromin and iodin compare with one another in stability as shown in their decomposition by the free halogens and by other agents? What is the action of their salts on the alkaloids? What substances liberate iodin from iodids and are therefore incompatible with these?

In what combination does hydrocyanic acid occur in plants and is it always poisonous in such form? In what

plants is it found ? How stable are solutions of the acid or its salts ? Are any of the salts poisonous ? What are the most common compounds which may be oxidized by nitric acid ? Does it ever cause explosions thus, or form explosive compounds ? What is its action upon alkaloids ? What is the origin of the yellow color frequently seen in nitric acid ? Are the nitrates chemically similar to the free acid ? How do the properties of the chlorates compare with those of the nitrates ? With what class of substances are dry chlorates incompatible and why ?

What change is produced upon the tartrates by oxidizing agents and what is the effect upon the latter ? Where are tartrates and citrates used to prevent the precipitation of the bases by the alkalies ?

CHAPTER III. ORGANIC COMPOUNDS.

Benzine and Petroleum Ether.

THESE are mixtures of hydrocarbons of the marsh gas series, boiling between 55° and 75°. They do not crystallize by cooling to 0°, and are insoluble in water.

270. If dropped into a cooled mixture of one part concentrated sulphuric acid and three parts fuming nitric acid there is no discoloration or odor of bitter almonds.

271. Iodin dissolves in either to a violet solution.

Benzene (Benzol), C_6H_6.

A colorless liquid with a characteristic odor, boiling at about 80°, lighter than water and almost insoluble in it. At zero it solidifies to a crystalline mass.

272. Cool a mixture of concentrated sulphuric and nitric acids, 5 cc. of each, as with benzine (270) and slowly drop in 15–20 drops of benzene, keeping the liquid cool. Nitrobenzene, $C_6H_5NO_2$, is formed, a yellowish oil with the bitter almond odor.

273. Iodin dissolves in benzene to a blood-red solution.

Chloroform, $CHCl_3$.

A colorless, neutral liquid with characteristic odor, having a specific gravity of 1.5 and a boiling point of about 61°. It is almost insoluble in water.

274. A strip of filter paper moistened with chloroform burns with a green-edged, yellow flame.

275. A drop of chloroform should not be rendered milky by a drop of silver nitrate (239).

276. With several times its volume of alcohol and a few

drops of sodium hydrate it is decomposed by warming into salts of hydrochloric and formic acid.

$$CHCl_3 + 4NaOH = 3NaCl + 2H_2O + HCO_2Na.$$

This solution gives a white precipitate with silver nitrate after acidifying with nitric acid (239).

277. To a solution of potassium hydrate in alcohol add a drop of anilin and one of chloroform and warm gently. Phenyl carbylamin, isonitril or isocyanid, C_6H_5NC, is formed, recognizable by its offensive odor.

278. With a few crystals of beta-naphtol and a few drops of sodium hydrate chloroform gives a blue color when warmed slightly. When only a minute quantity is present the blue may be transient.

279. In a 10 cc. dry test-tube place 5 cc. of chloroform and add without agitation 5 cc. of perfectly clear barium hydrate solution. After the corked tube has stood six hours in a dark place there should be no turbidity at the line of contact of the liquids (absence of decomposition products in chloroform which is otherwise pure).

280. Sodium hydrate with a few drops of copper sulphate (Trommer's reagent) gives a reddish-yellow precipitate when warmed with a drop of chloroform.

281. When shaken with one-fourth its volume of concentrated sulphuric acid and allowed to stand, pure chloroform is not colored yellow or brown.

282. When pure chloroform has been thoroughly shaken with an equal volume of water the latter, after pouring off, does not affect litmus paper, is unchanged with silver nitrate and gives no color with a few drops of potassium iodid and starch solution (244).

Iodoform, CHI_3.

Yellow crystals with a characteristic odor. It is almost insoluble in water but dissolves in alcohol or ether.

283. A drop of the alcoholic solution allowed to evaporate on a microscope slide leaves the iodoform in flat, hexagonal or star-shaped crystals, as is shown by the microscope.

284. The dry substance when heated in a test-tube melts at about 115° to a brown liquid and afterwards gives off the violet vapors of iodin, leaving a charred mass. The latter is completely combustible on a platinum foil.

285. Water which has been shaken with one-fifth its weight of pure iodoform and filtered is colorless, neutral, has no bitter taste and is unaffecteed by silver nitrate.

Ethyl Alcohol, C_2H_5OH.

A colorless, neutral liquid with a specific gravity of 0.79 and a boiling point of 78°.

286. 1 cc. of alcohol with an equal volume of stong sulphuric acid and a few crystals of sodium acetate gives, when heated to the boiling point, ethyl acetate, $C_2H_5C_2H_3O_2$ (acetic ether), which distils with a pleasant fruity odor.

287. With enough sodium hydrate to make it alkaline, then a solution of iodin and potassium iodid until it has a yellow color, followed by gentle warming, there forms, immediately or after short standing, a light yellow precipitate of iodoform (page 130). This reaction is a very sensitive one. It is also given by aceton, acetic aldehyd and some other organic compounds, but not by methyl alcohol.

288. If enough potassium dichromate is added to color the alcohol light yellow, and if it is then acidified quite strongly with sulphuric acid it is reduced to a chromic salt by boiling and this colors the liquid green. This is not characteristic of alcohol as other reducing agents may produce the same effect.

289. 10 or 12 drops of alcohol with 2 or 3 of carbon bisulphid and a little strong sodium hydrate produces a yellow sodium xanthogenate.

$$CS_2 + NaOH + C_2H_5OH = H_2O + NaSCSC_2H_5.$$

This with an aqueous solution of ammonium molybdate (1:10), after acidifying with sulphuric acid, gives a red color. To obtain it with dilute alcoholic solutions a few drops can be well mixed with one of carbon disulphid and a very small piece of sodium hydrate or potassium hydrate; after standing in an evaporating dish at the ordinary temperature until the carbon disulphid has disappeared a drop of the ammonium molybdate is to be added and enough sulphuric acid to acidify.

290. Pure alcohol (U. S. P.) should mix with water, ether and chloroform without cloudiness. It does not affect the color of litmus paper and leaves no residue upon evaporation; if it evaporates spontaneously from a paper no foreign odor should be perceptible. With half its volume of potassium hydrate solution it should not at once become dark colored nor should silver nitrate give more than a faint opalescence nor more than a faint brownish tint when standing six hours in diffused daylight.

Amyl Alcohol, $C_5H_{11}OH$.

A colorless liquid with a specific gravity of 0.82, and a boiling point of 131°. It dissolves in alcohol but not in water. It has a peculiar odor, its vapor causing coughing.

291. In alcoholic fluids any considerable quantity of amyl alcohol can be detected by means of its odor by pouring into a large beaker, spreading it over the sides, and causing the ethyl alcohol to evaporate quickly by swinging through the air. Evaporation on a water-bath also removes the water and ethyl alcohol and leaves the amyl alcohol.

292. From solutions of amyl alcohol in ethyl alcohol and water the former can be separated by its dissolving in ether or chloroform when shaken gently with these. It is left

when the ether or chloroform are poured off and evaporated, and can then be identified by its characteristic reactions.

293. If hydrochloric acid is dropped into a 1-per-cent. solution of methyl violet until it becomes green, then amyl alcohol is mixed with it in a porcelain dish, there appear on the top of the liquid violet drops.

294. Amyl alcohol dropped into 1 cc. of concentrated sulphuric acid gives a red color.

Glycerin, or Glycerol $(C_3H_5OH)_3$.

A neutral, colorless, odorless, syrupy liquid of a specific gravity of 1.25 to 1.27, with a sweet taste. It is hygroscopic and dissolves in water or alcohol.

295. A borax bead dipped in a solution which contains glycerin colors the blue flame of the Bunsen burner green (199).

296. Glycerin prevents the precipitation of copper, lead or ferric solutions by the alkaline hydrates.

297. Five drops each of glycerin and concentrated sulphuric acid gently warmed with as much resorcin as can be taken up on the point of a knife-blade gives first a crimson, then a blood-red color. Too high heat causes charring. When diluted with 5 cc. of water and made alkaline with ammonium hydrate the yellow solution shows a green fluorescence.

298. Pure glycerin will give no precipitate when tested by Trommer's test (280).

299. Pure glycerin when warmed gently with an equal volume of concentrated sulphuric acid or sodium hydrate is not colored dark.

300. An ammoniacal solution of silver nitrate is not changed when warmed with pure glycerin but upon the addition to it of sodium hydrate black metallic silver separates immediately.

Phenol (Carbolic Acid), C_6H_5OH.

Pure phenol is a colorless, crystalline solid with a characteristic odor. It melts at about 40° and dissolves in water to a neutral solution. The melted phenol solidifies upon cooling but the addition of a little water prevents this. An aqueous solution may be used for testing.

301. Neutral ferric chlorid solution, not in excess, produces a deep violet color which is changed to a yellow with hydrochloric acid.

302. Bromin water precipitates first white, then yellow tribromphenol, $C_6H_2Br_3OH$, soluble in alkaline hydrates or hydrochloric acid.

303. A solution of phenol in water made alkaline with a drop of ammonium hydrate becomes blue when warmed with a few drops of bromin water.

304. Five cc. of an aqueous solution boiled with 5 or 6 drops of concentrated nitric acid forms a brownish or yellow compound, picric acid, $C_6H_2(OH)(NO_2)_3$, which colors a large amount of water. The color is intensified by making it alkaline with ammonium hydrate.

305. A phenol solution with a drop of anilin, then an excess of a solution of calcium hypochlorite gives a deep blue color. (Anilin and calcium hypochlorite give a red.)

Creosote.

This is a colorless or yellowish liquid with a smoky odor, not solidifying in the cold and but slightly soluble in water.

306. Ferric chlorid colors the aqueous solution yellowish-green or a blue which quickly vanishes.

307. Bromin water gives a brownish precipitate.

Formaldehyd (Formalin), HCHO.

A colorless gas with a very irritating odor. It dissolves in water and is commonly to be obtained in the form of a

40-per-cent. solution. By concentrating the aqueous solution the aldehyd becomes converted into the solid paraformaldehyd, $(HCHO)_3$.

A 1-per-cent. solution can be used for the tests.

308. Silver nitrate, to which enough ammonium hydrate has been added to dissolve the precipitate first formed, is reduced by formaldehyd to metallic silver when allowed to stand several hours in a dark place, the metal being deposited as a mirror. If warmed this occurs immediately.

309. Formaldehyd reduces a solution of copper sulphate made alkaline with sodium hydrate with the formation of a reddish-yellow precipitate of cuprous oxid (Trommer's reaction.)

310. To a dilute fuchsin solution acidified with sulphuric acid add just enough sodium sulphite to decolorize it. Formaldehyd produces a purplish-violet color when warmed with this.

311. Formaldehyd gives a yellowish precipitate when it is warmed with phenyl-hydrazin hydrochlorid; this is the hydrazon, $C_6H_5NHNCH_2$.

312. A few cubic centimeters of a dilute formaldehyd solution with about 50 mg. of resorcin and half its volume of 50-per-cent. sodium hydrate, when warmed, is turned first yellow, then red. It is a very sensitive test.

313. Ammonium hydrate converts a solution of formaldehyd in solution into hexa-methylen-tetra-amin, which remains as a solid after evaporation.

314. A solution of 40–50 per cent. of sodium hydrate and 5 per cent. of resorcin in water when boiled half a minute with an equal volume of a dilute formaldehyd solution gives a red color. Albuminous compounds prevent the reaction.

315. Fifteen cc. of a very dilute solution of formaldehyd with 1 cc. of a dilute solution of phenyl-hydrazin hydro-

chlorid and a few drops of a freshly prepared solution of sodium nitroprussid when made alkaline with sodium hydrate becomes blue and, after long standing, red. Chloroform gives a similar result, but only in a much stronger solution, where it can usually be identified by its odor. If to the mixture of formaldehyd and the phenyl-hydrazin salt ferric chlorid is added, then the liquid strongly acidified with concentrated hydrochloric acid a red color forms, very slowly changing to orange-yellow. Both these tests can be made on milk directly without distillation and both are very sensitive.

315*a*. If 2–3 cc. of concentrated sulphuric acid is slowly added to the same volume of a formaldehyd solution so as to sink below it, a blue color appears between the liquids. The test is sensitive and can be used with milk. If no formaldehyd is present a brown color is produced.

Chloral Hydrate, CCl_3CHO,H_2O.

Colorless crystals with a sharp odor, soluble in water or alcohol to a neutral solution, melting at 57° and boiling at 98°.

316. When warmed with alkaline substances chloral hydrate is decomposed with the formation of chloroform. The latter may be detected by its odor or by the reactions for chloroform in the presence of an alkali (276, 277).

317. Chloral hydrate gives no precipitate with silver nitrate, but if it is allowed to stand for a time with dilute sulphuric acid and zinc, silver nitrate being subsequently added, silver chlorid is precipitated.

318. From an ammoniacal solution of silver nitrate chloral hydrate precipitates dark-brown metallic silver, slowly at the ordinary temperature, more rapidly on warming.

319. A chloral hydrate solution with as much resorcin as can be held on the point of a pen-knife and five drops of sodium hydrate gives an intense red color which is destroyed by hydrochloric acid.

320. Chloral hydrate with ammonium sulphid gives an orange color then a brown, more quickly on warming.

321. Pure chloral hydrate should not give the iodoform reaction (287).

Benzoic Acid, $C_6H_5CO_2H$.

Colorless needle-shaped or tabular crystals with an aromatic odor, melting at 121°, soluble with difficulty in cold water but easily in warm water, soluble in alcohol, ether and chloroform.

322. When heated in a dry tube the crystals melt and volatilize without blackening, becoming condensed in the crystalline form on the cooler part of the tube.

323. Benzoic acid dissolves in sulphuric acid without charring.

324. Lead acetate precipitates white lead benzoate, $Pb(C_6H_5CO_2)_2$, soluble in much boiling water and reprecipitated on cooling.

325. Ferric chlorid precipitates flesh-colored basic ferric benzoate, $Fe_2(C_7H_5O_2)_3(OH)_3$. Tartaric or citric acid prevents this.

Salicylic Acid, $C_6H_4OHCO_2H$.

Colorless, odorless, needle-shaped crystals, only slightly soluble in cold water, more soluble in hot water. The normal salts are soluble in water, the basic ones less so. From these solutions the free acid is precipitated by mineral acids.

326. When slowly heated salicylic acid melts at 156° and sublimes as white crystals; by rapid and high heating it decomposes into carbon dioxid and phenol, the latter recognizable by its odor.

327. Ferric chlorid gives a deep reddish-purple color. Mineral acids, bases and some salts may prevent the formation.

328. Salicylic acid, or the salicylates, dissolved in 1 cc. of methyl alcohol, when 1 cc. of concentrated sulphuric is

added and the mixture warmed, will produce methyl salicylate, $C_6H_4(OH)(CO_2CH_3)$, oil of wintergreen. Ethyl alcohol gives ethyl salicylate in the same manner, having a very similar odor.

329. Salicylic acid gives similar reactions to phenol with boiling nitric acid (304), and bromin water (302).

330. Concentrated sulphuric acid makes a colorless solution with salicylic acid when cold, turning brown upon warming.

Meconic Acid, $C_5H_2O_3(CO_2H)_2$.

331. Meconic acid is a white crystalline solid, soluble with difficulty in cold water, but readily so with warming, also soluble in alcohol.

332. Ferric chlorid imparts a blood-red color to a solution of meconic acid. This is not discharged by boiling (259), by acidifying with hydrochloric acid (259), nor by mercuric chlorid (229). Stannous chlorid decolorizes it.

333. Silver nitrate produces a yellowish precipitate, becoming a brighter yellow when it is warmed.

Tannic Acid or Tannins.

There are a number of tannins with similar properties. They are yellowish powders, soluble in an equal weight of water, also in alcohol or glycerin, and turning litmus paper red.

334. Solutions of tannic acid, when made alkaline, rapidly absorb oxygen, becoming red, brown or black.

335. Ferric salts produce a blue-black color or precipitate, which is prevented or destroyed by acids.

336. Lime-water produces a bluish-white precipitate, becoming darker blue as the amount of the reagent is increased and finally changing to a pinkish color.

337. Tannic acid reduces a permanganate solution.

338. Solutions of albumin, gelatin or starch are precipitated by tannic acid.

339. A solution of iodin in potassium iodid to which enough potassium cyanid has been added to produce a colorless liquid gives a red color with tannic acid. An excess of the cyanid deepens the color. It changes in one or two minutes to brown.

340. A solution of antimony potassium tartrate precipitates a tannic acid solution.

341. Tannic acid precipitates most alkaloids.

Gallic Acid, $C_6H_2(OH)_3CO_2H$.

A white or yellowish, crystalline powder, soluble in 100 parts of water, also in alcohol or glycerin. It has an acid reaction.

342. When made strongly alkaline solutions of gallic acid become yellow, red and brown through the absorption of oxygen. If the alkali is not in excess the solution slowly turns green.

343. Ferric salts give a bluish-black color or precipitate with gallic acid solutions.

344. Lime-water gives a bluish precipitate, as the reagent is increased becoming darker blue in color by reflected light and a greenish by transmitted light, with a large excess changing to a pink color.

345. A permanganate solution is reduced by gallic acid.

346. Solutions of albumin, gelatin or starch are not precipitated by gallic acid.

347. Gallic acid does not precipitate the alkaloids.

348. With a solution of iodin in potassium iodid which has been decolorized by potassium cyanid, gallic acid gives a red color, changing to yellowish-brown. The latter change is slower than with tannic acid (339).

Starch, $(C_6H_{10}O_5)_x$.

It is found in vegetable substances in the form of granules, those of one species of vegetable often differing suf-

ficiently from those of another to render possible the determination of their source by microscopic examination. It is insoluble in cold water, neutral and tasteless. The granules are destroyed by heating with water, the starch forming a semi-soluble paste. This may be used for the tests.

349. With a solution of iodin starch gives a dark-blue color. This is decolorized by alkalies or by heating. In the latter case when the liquid cools it becomes colored again. The dry starch is colored by the same reagent.

350. When boiled some time with a dilute mineral acid starch is converted into glucose, $C_6H_{12}O_6$. The liquid then forms no blue compound with iodin.

Glucose (Grape Sugar), $C_6H_{12}O_6$.

This is to be obtained as a dry solid or as a colorless syrup. Its taste is less sweet than that of cane sugar. It is readily soluble in water.

351. A solution of glucose when made alkaline with sodium hydrate and into which copper sulphate has then been dropped gives on warming a reddish-yellow precipitate of cuprous oxid, Cu_2O. (Trommer's reaction.)

352. A glucose solution when heated 15 minutes with as much phenyl-hydrazin hydrochlorid as can be taken up on the point of a knife-blade and twice as much crystallized sodium acetate will, on cooling, deposit bright yellow crystals of phenyl-glucosazone, best observed with the microscope.

353. Mixed with a small piece of compressed yeast and placed in an inverted test-tube, standing at a temperature of 40° with the mouth under some of the same solution, the glucose ferments to carbon dioxid, which rises in the tube and can be tested by lime-water (185). Alcohol (287) is formed at the same time.

354. When warmed with glucose an ammoniacal solution of silver nitrate is reduced with the deposition of metallic silver.

355. Concentrated sulphuric acid does not blacken dry glucose in the cold.

Saccharose (Cane Sugar), $C_{12}H_{22}O_{11}$.

Colorless, odorless, sweet crystals, neutral in reaction.

356. With Trommer's reagent (351) cane sugar gives no precipitate by heating to the boiling-point, although it may do so by long continued heating.

357. Boiling with dilute mineral acids changes cane sugar into glucose which may be detected in the above manner after neutralizing (351).

358. With phenyl-hydrazin saccharose reacts like glucose (352).

359. An aqueous cane sugar solution (1 : 10) when quickly heated to boiling with an ammoniacal solution of silver nitrate then allowed to cool should give no more than a faint coloration, but no dark precipitate, in five minutes.

360. Concentrated sulphuric acid turns dry cane sugar yellow, brown and at last black without the application of heat.

Lactose (Milk Sugar), $C_{12}H_{22}O_{11}$.

White, hard crystals with a somewhat gritty, sweetish taste, less soluble in water than glucose or saccharose.

361. Lactose gives the same results as glucose with Trommer's reagent (351).

362. Yeast does not produce the fermentation of lactose (353).

363. Concentrated sulphuric acid in the cold does not blacken dry milk sugar.

364. Lactose with phenyl-hydrazin (352) and Trommer's

reagent (351) gives similar results to those obtained from glucose.

Antipyrin (Phenyl-di-methyl-pyrazalon), $C_6H_5(CH_3)_2C_3N_2HO$.

Colorless, odorless crystals with a bitter taste. It unites with acids, as do the alkaloids, to form salts but has no alkaline reaction to litmus. It melts at 113° and blackens at higher temperatures. It is precipitated by most of the general alkaloidal reagents (page 144).

365. Concentrated sulphuric acid dissolves antipyrin to a colorless solution, not darkened by heating.

366. A solution of antipyrin in water when made strongly acid with nitric acid and warmed turns yellow, then red.

367. The solution in water with a few drops of fuming nitric acid becomes emerald green; with a larger amount of the acid it turns red. A nitrite added to a slightly acidified solution of antipyrin also gives the same green color.

368. The aqueous solution of antipyrin is colored red by a drop of ferric chlorid, becoming yellow with sulphuric acid.

369. Mercuric chlorid gives a white precipitate, readily soluble on warming and reprecipitating as the solution cools.

Acetanilid (Antifebrin), $C_6H_5NHCH_3CO$.

A cororless, odorless, nearly tasteless, crystalline substance, soluble with difficulty in cold water but easily soluble in hot water or alcohol. It melts at 113°.

370. Acetanilid dissolves in either concentrated sulphuric or nitric acid without discoloration.

371. When heated with sodium hydrate acetanilid is decomposed with a formation of anilin which gives its characteristic odor. If then a few drops of chloroform are added and the mixture heated it gives isonitril (277).

372. One cc. of hydrochloric acid warmed with a little acetanilid decomposes the latter into anilin and acetic acid. If a drop of phenol is added, and a little calcium hypochlo-

rite solution, the liquid becomes reddish. When made alkaline with ammonium hydrate this changes to a blue (indophenol reaction).

373. Ferric chlorid produces no color with acetanilid beyond the yellow of the reagent. When warmed this becomes darker.

374. Warmed with 1 cc. each of strong sulphuric acid and alcohol the odor of ethyl acetate (286) appears.

Phenacetin (Para-acet-phenetidin), $C_2H_5OC_6H_4NHCH_3CO$.

Colorless, odorless, almost tasteless crystals, soluble in hot water or alcohol, almost insoluble in cold water. It melts at 135° and sublimes at a higher temperature with white fumes.

375. Concentrated sulphuric acid does not discolor phenacetin.

376. Warmed with concentrated nitric acid a yellow or orange color appears.

377. Phenacetin does not give the isonitril reaction (277) except after long heating, as it decomposes much more slowly than acetanilid (371).

378. Phenacetin gives the indophenol reaction like acetanilid (372).

379. Ferric chlorid gives a yellow color on heating.

380. When heated with concentrated sulphuric acid and alcohol, phenacetin gives ethyl acetate (374).

381. 0.1 grm. of phenacetin warmed one minute with concentrated hydrochloric acid, then diluted to 10 cc., on the addition of three drops of potassium dichromate solution gives a reddish-violet color.

Salol (Phenyl Salicylate), $C_6H_4OHCO_2C_6H_5$.

A colorless, crystalline powder with an aromatic odor, insoluble in water but soluble in alcohol. It melts at 42°; in hot water it goes to the bottom in oily drops.

382. When warmed with water and a few drops of sodium hydrate it dissolves with decomposition. From this solution hydrochloric acid precipitates the salicylic acid as a white solid and the phenol can be recognized by its odor.

383. Equal parts of salol and potassium nitrate mixed with 1 cc. of concentrated sulphuric acid form a bright greenish-blue liquid. On dilution with water or through standing in the air it passes into red and fades. Sulphuric alone produces no change.

384. From the alcoholic solution bromin water precipitates white monobromsalol.

385. On adding to an alcoholic solution of salol a few drops of a very dilute (straw-yellow) solution of ferric chlorid a violet or purple color appears; if the salol solution is dropped into the iron solution there is a white precipitate but no color.

386. After shaking with water and filtering, the filtrate should give no result with ferric chlorid (301, 327), barium chlorid (178, 202) nor silver nitrate (239).

Sulphonal (Di-ethyl-sulphon-di-methyl-methan), $(C_2H_5SO_2)_2C(CH_3)_2$.

Colorless, odorless, tasteless crystals, soluble with difficulty in cold water but readily by the aid of heat, also in alcohol. It melts at 126°.

387. On platinum foil sulphonal burns with a yellow flame and the odor of sulphurous oxid.

388. If sulphonal is mixed with ten times its bulk of powdered charcoal and the mixture heated to redness in a dry tube it gives off the garlicky odor of mercaptol. Acetic acid and sulphurous oxid are formed also. If instead of charcoal the sulphonal is fused with potassium cyanid mercaptol is formed and also potassium sulphocyanate, the

latter being found in the aqueous solution by the use of ferric chlorid after filtering (229).

389. Sulphonal is not decomposed by mineral acids, alkalies nor the halogens.

The Alkaloids.

The alkaloids are a class of vegetable nitrogenous compounds which are chemically similar to ammonia. Like this the free alkaloids are of a basic nature and they form salts by uniting with acids without the setting free of hydrogen. Only a few of the alkaloids are liquid most of them, as well as their salts, being crystallizable solids. Their salts are, as a rule, much more easily soluble in water than the alkaloids themselves. They are decomposed by alkalies, the alkaloid being set free, just as ammonia is freed from its salts by the same reagents. When it is in a concentrated solution this process often results in their precipitation as the alkaloid is less soluble than its salts. There is a great difference in the comparative solubility of the alkaloids in many of the organic liquids like chloroform, benzene, ether, petroleum ether, amyl alcohol, etc., and the methods devised for their separation are based upon this. They all have a bitter taste, as do their salts. The separation and identification of the alkaloids is not as simple an operation as in the case of the metallic compounds.

There are a number of reagents which will precipitate most or all of the alkaloids and these are of value in proving the presence or absence of the class, although the results are often so similar that they cannot be used for the identification of the individual members. Among the most important of these alkaloidal group reagents are:

Tannic acid, which precipitates most alkaloids, as well as some other similar substance, as white or yellow-

ish, flocculent compounds. They are often soluble in excess of the precipitant or in other acids.

Picric acid, which from not too dilute solutions precipitates yellow compounds, often crystalline in form.

Phosphomolybdic acid precipitates the alkaloids and similar nitrogenous compounds in the form of yellowish, or brownish-yellow, solids. These can be filtered from the solution and the alkaloid set free from them by the alkalies and their carbonates.

Phosphotungstic acid acts like the phosphomolybdic in most cases.

Mercuric potassium iodid precipitates most alkaloids from solutions of their sulphuric or hydrochloric acid salts as white or yellow compounds.

Iodin in potassium iodid forms brown precipitates with alkaloidal solutions.

Mercuric chlorid, *platinic chlorid* or *gold chlorid*, from not too dilute solutions, throw down white, or yellowish, precipitates. With dilute solutions they may only form a turbidity.

In order to identify a compound as an alkaloid it must not only give the general tests for the class but be characterized by some special reaction or reactions. In the special reactions that follow it may be assumed, unless it is otherwise stated, that the alkaloid under discussion will, in the main, give the general reactions.

In the reactions of the alkaloids, and in others where it often becomes necessary to identify minute quantities of material, it is convenient, instead of test-tubes, to make use of small, rather flat, watch crystals. The results of the treatment of a drop of solution with one of the reagent are plainly perceptible if the watch-glass stands upon a suitably colored paper, and the precipitate can be examined with the microscope, placing the watch-glass upon the stage. If it

is desired to make the test upon a solid compound the drops of solution on the watch-glass may be evaporated to dryness on the steam-bath. At first rather large amounts of the alkaloids may be used but after some skill has been gained this should be reduced to very minute quantities in order to show the sensitiveness of the reagents.

Morphin, $C_{17}H_{19}NO_3$.

Morphin and its sulphuric and hydrochloric acid salts are white compounds crystallizing in needles or prisms.

390. Concentrated nitric acid dissolves morphin or its salts with a blood-red color which gradually passes into a yellow. The latter is not changed to a violet by addition of stannous chlorid, but is colored reddish-brown. Only a small amount of the acid should be used.

391. Concentrated sulphuric acid dissolves morphin to a colorless liquid. If to this a trace of nitric acid is added there is no change in color, but if it has stood 24 hours, or is heated to 100° for half an hour, the nitric acid produces a red. A crystal of potassium permanganate added to the sulphuric acid solution should produce no violet or purple color.

392. Fröhde's reagent gives a violet solution, gradually changing to brown, green and yellow.

393. A neutral solution of ferric chlorid with morphin or solutions of its neutral salts gives a blue color. Only a small quantity of the ferric compound can be used as an excess prevents the reaction. The color is destroyed by free acids, and impurities may prevent its appearance. The ferric chlorid, which ordinarily has an acid reaction, must be prepared by subliming the crystals in a hard-glass tube after driving off the water and acid by gentle heating; then dissolve the sublimate in distilled water. The solution should be nearly or quite neutral. Impurities may prevent

the formation of the color. The correctness of the reagent must be proved by its ability to produce the blue with a specimen of pure morphin sulphate. Some ptomains give a greenish color, but not a blue. None of the other vegetable alkaloids give this result.

394. Morphin with half its weight of sugar gives a red color to a drop of concentrated sulphuric acid.

395. Vanadium sulphate produces a reddish, then a violet color.

Narcotin, $C_{22}H_{23}NO_7$.

Concentrated sulphuric acid dissolves narcotin to a colorless liquid. If the acid contains a trace of nitric acid, as happens often with the ordinary chemically pure acid, the solution turns yellow on standing and red by warming. The red is easily obtained by dissolving in a little dilute acid, then evaporating from a test-tube very slowly by means of a small flame. After the red liquid cools a trace of nitric acid changes it to violet.

396. Concentrated nitric acid dissolves narcotin to a yellow solution.

397. Fröhde's reagent of the ordinary strength dissolves narcotin, forming a green solution. If stronger (0.01 gm. molybdate in 1 cc. of acid) the green solution soon changes to a cherry red.

398. Erdmann's reagent gives a red solution.

399. Vanadium sulphate gives a red color likewise.

Strychnin, $C_{21}H_{22}N_2O_2$.

Strychnin is soluble with difficulty in water, its salts much more easily so. It is one of the most intensely bitter alkaloids. It gives reactions in very dilute solutions with most of the general alkaloidal reagents. The chlorids of gold and platinum do not react in very dilute solutions, perhaps below 0.1 per cent. to 0.01 per cent.

400. Strychnin forms a colorless solution with concentrated sulphuric acid.

401. To the dry substance add a drop of strong sulphuric acid, about one part water to five parts of acid, then by means of a glass rod, draw through the solution a minute crystal of potassium dichromate. A series of colors results, always in the same order; first blue which quickly becomes violet, then more slowly red, pink and yellow. The colors are characteristic of strychnin and, when the substance is pure will be produced by as small an amount as the fifty-thousandth of a grain. The reaction is, however, interfered with by the presence of a number of organic compounds, including morphin. Potassium permanganate gives similar results when used instead of the dichromate.

402. Vanadium sulphate solution dissolves the solid compounds with the production, first of a blue, followed by a violet and red color. If it is then diluted with water the pink remains for a long time.

403. Cerium oxid with strychnin in concentrated sulphuric acid gives the same colors as the last reagent. It will react with the millionth of a gramme. To make the reagent heat cerium oxalate to redness to form the oxid and dissolve this in thirty times its weight of concentrated sulphuric acid.

404. Strychnin gives no color when treated with concentrated sulphuric acid and a molybdate, nitrate or nitric acid.

405. Concentrated nitric acid colors strychnin or its salts only faintly yellow, if at all, when it dissolves them, but on standing the solution becomes a darker yellow.

Brucin, $C_{23}H_{26}N_2O_4$.

The alkaloid and most of its salts are crystalline.

406. Concentrated nitric acid dissolves brucin to a deep red liquid, which on standing or heating becomes yellow.

After this has occurred dilute the solution and with this a reducing agent, like stannous chlorid, will give a violet. An excess of nitric acid must be avoided or the reaction loses in sensitiveness. The violet solution when made alkaline with sodium hydrate changes to blue or green. These changes are peculiar to brucin.

407. Concentrated sulphuric acid dissolves brucin without producing a color.

408. Chlorin water forms a bright red solution, the color being destroyed by an excess of the reagent and turned brownish-yellow by ammonium hydrate.

Atropin, $C_{17}H_{23}NO_3$ (Daturin).

409. Atropin imparts a color to neither concentrated nitric nor sulphuric acid in the cold but dissolves to a clear solution.

410. A crystal of atropin when moistened with three or four drops of fuming nitric acid leaves a yellowish residue when evaporated to dryness on a steam-bath. Let a drop of a solution of potassium hydrate in 90-per-cent. alcohol run over the residue. Where they come in contact a reddish-violet color is produced.

411. If a milligramme of atropin is heated in a dry test-tube until vapors begin to appear and then 1 cc. of concentrated sulphuric acid is added and the heating continued the odor of flowers is observed. By cautiously diluting with 2 cc. of water and warming further it may be made more distinct. On addition of small crystals of potassium dichromate to the concentrated acid solution the odor changes to that of oil of bitter almonds.

412. Platinic chlorid does not precipitate atropin or its salts.

413. A very dilute aqueous solution of atropin (1 : 100,000) when applied to the eye causes a dilation of the pupil which lasts for a long time.

Veratrin.

414. Veratrin dissolves in concentrated sulphuric acid which is free from nitrogen compounds to a colorless solution. On warming it changes to a crimson-red. In the ordinary chemically pure acid it makes a yellow solution, changing to an orange, then blood-red and in half an hour, to a carmine-red. The addition of a minute quantity of nitric acid hastens these changes.

415. When warmed a few minutes in a small test-tube with 1 cc. of concentrated hydrochloric acid the latter is colored a reddish-violet. No other alkaloid gives this reaction.

416. If mixed with 2 to 4 times the amount of cane sugar, then moistened with concentrated sulphuric acid (only a little being added from a glass rod, not enough to make a solution) veratrin gives a dark green color, becoming purple and then blue in a few minutes. From the action of the acid on the sugar it finally turns brown and black.

Cocain, $C_{17}H_{21}NO_4$.

417. Solutions of the alkaloid or its salts in water cause numbness when applied to the tongue and dilation of the pupil when applied to the eye.

418. Concentrated sulphuric acid dissolves the cocain or its salts without discoloration. When warmed it turns brown, the hydrochlorid giving the odor of hydrochloric acid.

419. Concentrated nitric acid gives no color with cocain in the cold.

420. With 1-per-cent. solution of potassium permanganate cocain yields a precipitate of cocain permanganate. This upon standing collects in radiating clusters of thin tabular crystals, a bright reddish-purple in color, very plainly to be seen with a low power of the microscope.

421. An aqueous solution of cocain acidulated with dilute sulphuric acid, to which enough potassium permanganate solution has been added to give a pink color, does not lose this after standing half an hour at the ordinary temperature.

422. If a little cocain hydrochlorid is powdered with as much mercurous chlorid in a dry porcelain dish the mixture is white but it becomes gray in presence of a little moisture, even by being breathed upon.

423. Cocain or its hydrochlorid when evaporated to dryness on the steam-bath, after the addition of 1 cc. of concentrated nitric acid, leaves a colorless residue. With a few drops of alcoholic potassium hydrate it develops the pleasing and permanent odor of benzoic ethyl ester. No purple color is thus produced, as with atropin (410).

424. Cocain hydrochlorid solution with a few drops of potassium dichromate gives a yellow precipitate which quickly disappears. On acidifying the solution then with hydrochloric acid an orange-yellow crystalline precipitate of cocain chromate appears which is soluble in excess of the acid.

Quinin, $C_{20}H_{24}N_2O_2$.

425. Quinin or its salts give no color with Erdmann's reagent, Fröhde's reagent or with concentrated nitric acid.

426. Solutions of quinin, as well as many salts of quinin, after acidifying with sulphuric acid, give a bluish fluorescence, perceptible in very dilute solutions and a characteristic reaction. Concentrated acid dissolves the dry alkaloid to a similar fluid, with no brown or black color.

427. Ten cc. of a solution of a quinin salt in water with two drops of bromin water or chlorin water and enough ammonium hydrate to render it alkaline gives an emerald-green color.

If to the solution in dilute sulphuric acid the chlorin water is added as before, then two drops of potassium fer-

rocyanid solution, and afterwards enough ammonium hydrate to make it alkaline, a red color appears which disappears on standing. No other alkaloid gives the last two reactions.

428. If to an alcoholic solution of quinin sulphate there is added tincture of iodin, and the mixture is warmed, then allowed to stand and cool, there separates a precipitate consisting of clusters of crystals, dark-green by transmitted light and with a metallic luster by reflected light. The compound is called herapathit and is characteristic of quinin.

Questions for Further Study on Organic Compounds.

What are organic substances and how distinct is the line between these and the inorganic? Are benzene and benzine easily combustible? Why? What is the nature of substances of which the vapors form explosive mixtures with air? What is the difference in arrangement of atoms in the molecules of the above compounds? Under what circumstances is iodoform decomposed by air or light? What oxidizing agents oxidize alcohol or its solutions? What is produced by the action of strong mineral acids upon alcohol? Why do many tinctures give precipitates when diluted with water? Are there any which do not? Why? What compounds, organic and inorganic, are soluble in alcohol? In what beverages is amyl alcohol found and under what name? What is the value of glycerin as a solvent? Will carbolic acid neutralize solutions of the alkalies? With what solids does the crystallized substance form a liquid mass on trituration? For what is formaldehyde most extensively used? How can it be most readily generated? Where does meconic acid occur and what is its importance? What drugs contain a large proportion of tannic acid? Are the aqueous solutions of gallic

and tannic acid permanent? What would be the effect of triturating them dry with strong oxidizing agents? Is tannic acid incompatible with solutions of any other metals except antimony? Can starch be changed into glucose by other means than by mineral acids? What is the relation of this to "liver starch"? Does grape sugar occur elsewhere than in the grape? What are the best means of distinguishing the three kinds of sugar? What is the relation of the alkaloids to the ptomaines? Is there any similarity in their reactions? Which are the liquid alkaloids? With what solids does antipyrin give a liquid mass on trituration? What is the difference between an isonitril and the cyanid of an organic radical? What are the mercaptols? Trituration with what solids and salol gives a liquid mass?

PART II.

VOLUMETRIC ANALYSIS.

CHAPTER I. GENERAL PRINCIPLES.

In quantitative chemical analysis, that is, the determination of the amounts of the constituents of a compound or mixture, two methods may be employed, the gravimetric, where the constituent or some form of it is isolated and weighed, and the volumetric, where to a definite quantity of the substance there is added of a dissolved reagent just sufficient to complete some chemical change, such as precipitation, neutralization or oxidation. If the strength of this reagent is known we can calculate from the volume necessary for the reaction the weight of the compound acted upon.

For example the strength of a solution of silver which has been dissolved in nitric acid may be ascertained in two ways. We know that when the metal dissolves it forms silver nitrate, of which the formula is $AgNO_3$. Of this the atom of silver weighs 107.12, of nitrogen 13.94, and the three atoms of oxygen 47.637, or a weight of 168.697 for the molecule. If hydrochloric acid is added to this solution silver chlorid is produced.

$$\begin{array}{cccc} AgNO_3 + & HCl = & AgCl + & HNO_3. \\ 168.697 & 36.18 & 142.30 & 62.577 \end{array}$$

That is, one molecule of hydrochloric acid having a weight of 36.18 will convert 168.697 parts of silver nitrate into 142.30 parts of silver chlorid and 62.577 parts of nitric

acid. The silver chlorid, which forms a precipitate, can be filtered from the liquid, washed, dried and weighed. Since of every 142.30 parts of the chlorid there are present 35.18 of chlorin and 107.12 of silver a simple proportion will give the weight of silver in the compound. Thus

$$142.30 : 107.12 = \text{weight of AgCl} : \text{weight of Ag}.$$

This is the gravimetric method.

In the volumetric method the hydrochloric acid would be made of such a strength that each cubic centimeter would contain a known and definite weight of HCl. From the number of cubic centimeters of acid used and the strength of each we can calculate the weight of HCl necessary to precipitate the silver. A proportion gives the weight of silver precipitated, this being equal to 107.12 parts of silver for each molecule of HCl. Thus

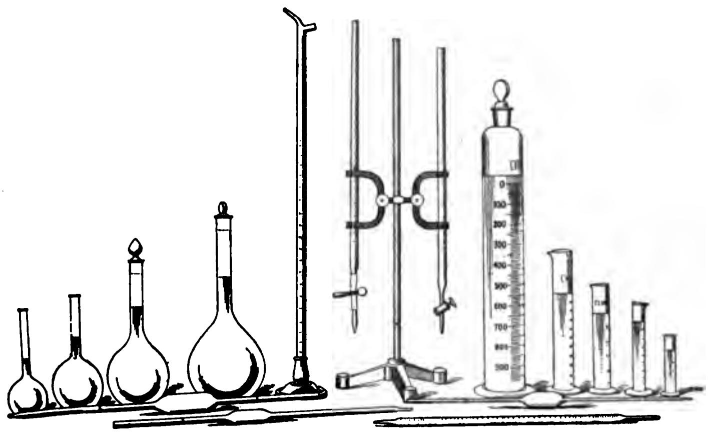
$$36.18 : 107.12 = \text{weight of HCl used} : \text{weight of Ag}.$$

Gravimetric methods require a considerable time for their completion and usually demand more manipulative skill than the volumetric. A very sensitive and somewhat expensive balance is also a necessity. On the other hand the volumetric methods can be easily and rapidly carried out after the standard solutions are prepared and the apparatus is neither dear nor cumbersome. In some cases, on account of the impossibility of deciding when the proper amount of the reagent has been used, volumetric methods of analysis must be abandoned. However, since they are so convenient of application, they will be the principal ones studied here.

The measuring apparatus employed in volumetric chemical analysis is for the determination of volume and it is graduated according to the metric system (see table, page 238) because of the great readiness by which calculations can be made thereby. The unit most in use is the cubic centimeter (cc.), with its divisions and multiplies.

Measuring cylinders are narrow cylinders of glass with a foot. On account of the comparatively large surface of the liquid, whereby a slight variation in the height of the liquid makes a considerable difference in its volume they can only be used where accuracy is not essential. They will, however, roughly measure any volume less than their

FIG. 13.



Apparatus for Measuring. 1. Flasks. 2. A pouring burette. (Bink's form.) 3. Two dropping burettes (Mohr's form) in a holder, one with a rubber tube and spring clamp, the other with a glass stop-cock. 4. Graduated cylinders. 5. In front are three pipettes with bulbs and one of the cylindrical form.

total capacity. Some are of the same diameter throughout their length and others are fitted with glass stoppers for convenience in shaking their contents.

If accurate measurements of comparatively large volumes are necessary flasks serve the purpose better. Accuracy is gained by a narrow neck where they are marked to indicate the height to which they should be filled. It is advantageous to have two marks, the lower one of which shows where the liquid should stand when the flask con-

tains the volume which it is designed to hold, for example, a liter, and the upper (but little above the first) to which the fluid must rise if the flask is expected to deliver a liter when it is emptied. That is, allowance is made for the few drops which adhere to the inside of the vessel. Measurements can by this means be made of only one volume and no fractional parts of it. Measuring flasks are used for the preparation of the standard solutions that are employed in volumetric analysis. As variations in temperature cause expansion and contraction in the liquids the volume will be correctly measured only at that temperature at which the flask was calibrated. This is usually at 15° C.

A pipette is a measure used to deliver a definite and fixed volume also. It is made of a glass tube, either with an expansion or bulb in the middle, or of the cylindrical form. To fill it the point is inserted in the liquid, then the air above is exhausted by the mouth until the liquid rises above the upper mark, when the tube is removed from the mouth and the top quickly covered with the forefinger. By slightly turning the finger the liquid, which should now stand above the mark, is allowed to flow out until the surface coincides with the mark. The pipette is then held over another vessel and the liquid is poured into this. Some pipettes have two graduation marks, one above the bulb and the other below. In this case the liquid must be allowed to escape only until it reaches the level of the lower one. If there is but a single graduation above the bulb, it should be emptied, and the last drop removed by touching the side of the vessel below. Pipettes of this shape are very accurate since the area of the tube is small as compared with that of the bulb. Each one will deliver only the volume for which it is calibrated. They are ordinarily not used for measuring over 100 cc. The cylindrical form allows the measurement of fractions of its whole

volume, being graduated throughout the greater part of its length. With the smaller sizes a rubber bulb, or nipple, slipped over the upper end enables the operator to regulate the flow to dropping or any desirable speed.

When measurements are to be made of varying volumes of liquid a burette should be employed. This is made of a cylindrical tube, carefully graduated into cubic centimeters and their fractions. It differs from the cylindrical pipette in not having its delivery regulated by the finger on the upper end. There are two varieties, the dropping and the pouring burettes. The flow from the former is usually regulated by a valve or stop-cock below. One with a glass stop-cock, although the most expensive, is preferable since rubber affects the strength of some solutions if allowed to remain in contact with them. (A little vaseline will prevent the stop-cock sticking.) Instead of this in many cases a short piece of rubber tubing can be slipped over the end of the burette and the amount of liquid delivered can be controlled by the compression of the tubing by a spring clamp or pinch-cock. A solid bead of glass slightly larger than the inside diameter will also close the tube when placed within it. By squeezing this between the thumb and forefinger the rubber is stretched and the contents of the burette slowly drop from the narrow jet below. Where frequent determinations are made with the same solution the lower part of the burette can be connected with the stock bottle of the same, thus permitting it to be filled without pouring into the top of the tube.

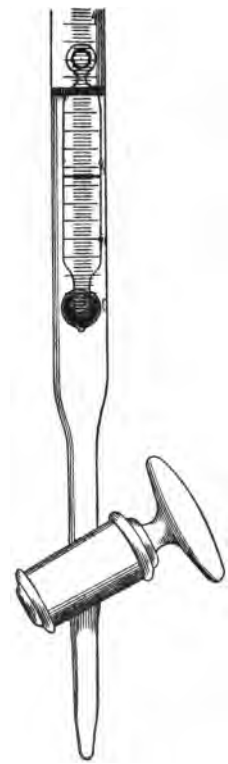
The pouring burettes vary somewhat in form, but are essentially a long, narrow tube graduated like the others but closed at the bottom. From these the solution is poured out of a small jet at the top, and the amount thus used is indicated by the difference between the height of the liquid before and after the pouring. By holding the finger over

the large tube to govern the admission of air the flow can be exactly regulated. They have no rubber parts to change the strength of the solutions used in them and do not cost as much as those with glass stop-cocks.

FIG. 14.

The lower part of a Mohr's burette with spring clamp, showing the meniscus.

FIG. 15.



The lower part of a Mohr's burette with glass stop-cock and Erdmann's float in the solution.

An examination of the surface of a liquid in a glass vessel, particularly if this is a narrow one, shows that the surface is not flat but concave or saucer-shaped. This is

called the meniscus. It results from the attraction between the glass and liquid which causes a rising of the latter at the circumference. When seen from the side it is sometimes a matter of uncertainty which part should be regarded as the top of the column. In measuring with a burette this is a matter of indifference providing the same part is always used. With deeply colored liquids only the upper line can be distinguished. With colorless ones the lower margin of the meniscus is most distinct, especially if a white card is held behind it. In all cases the eye of the observer must be on the same level as the meniscus. The Erdmann's float or swimmer may be employed as an aid in determining how much the column has fallen in the burette. This is a narrow tube weighted so as to float vertically in the burette. A line around the float is the measuring point instead of the meniscus.

The standard solutions employed in volumetric analysis are of two kinds, the normal and the empirical. A normal solution $\left(\frac{N}{1}\right)$ contains in one liter a number of grammes of the active reagent equal to its molecular weight, provided the molecular weight of the reagent is equivalent to one atom of hydrogen. Otherwise one liter contains such a fraction of the molecular weight as is the equivalent of one hydro gen atom. The valence of the radical or active component of the compound indicates the number of hydrogen atoms to which it is equivalent. For example,

Reagent.	Radical or Active Component.	Valence of Active Component.	Molecular Weight.	Normal Solution. Grammes per Liter.[1]
HCl	Cl	I	36.18	36.18
NaOH	Na	I	39.699	39.70
NH_4OH	NH_4	I	34.819	34.82
Na_2CO_3	Na_2	II	105.187	52.59
H_2SO_4	SO_4	II	97.336	48.62

[1] In making normal solutions, unless exceptional accuracy is required, the weighings do not need to be carried farther than two decimal places.

Reagent.	Radical or Active Component.	Valence of Active Component.	Molecular Weight.	Normal Solution. Grammes per Liter.
$H_2C_2O_4,2H_2O$	C_2O_4	II	125.094	62.55
H_3PO_4	PO_4	III	97.316	32.44
$2KMnO_4$	O_5[2]	V	156.886	31.38

Since there are 1,000 cc. in a liter each cubic centimeter of a normal solution contains as many milligrammes of the reagent as there are grammes in the liter. One cubic centimeter of a normal solution is the equivalent of one cubic centimeter of any other normal solution. This is illustrated by the following examples:

$$\underset{36.18}{HCl} + \underset{39.699}{NaOH} = NaCl + H_2O.$$

$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O.$$

$$\begin{array}{rl} 2)\underline{97.336} & \underline{79.398} \\ 48.668 & 39.699 \end{array}$$

$$2KMnO_4 + 5H_2C_2O_4,\ 2H_2O + 3H_2SO_4 =$$

$$\begin{array}{rl} 10)\underline{313.772} & \underline{625.470} \\ 31.377 & 62.547 \end{array}$$

$$K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O.$$

The equations represent the chemical actions taking place between different compounds, the numbers below giving the weight of the one or more molecules which enter into the reaction. In all cases these weights are seen to be in the same relation as those in the cubic centimeter of the normal solution, therefore equal volumes of such normal solutions are equivalent in their power.

In many determinations a normal solution is too strong for use and one of a fractional amount may be substituted. One tenth of the normal $\left(\text{decinormal, } \frac{N}{10}\right)$ or one hundredth the normal $\left(\text{centinormal, } \frac{N}{100}\right)$ are common. These

[2] $KMnO_4$ acts as an oxidizing, agent, two molecules yielding 5 atoms of oxygen.

are prepared by placing in a measuring flask one-tenth or one one-hundredth of its volume of the normal solution, then diluting to the mark. In the same manner others can be made if more convenient.

An empirical standard solution is not made up in the same manner as the normal but is represented by Fehling's solution for the determination of glucose and some other sugars. Enough copper sulphate is taken for 1 cc. to oxidize 0.005 grm. of glucose.

The operation of volumetric analysis is called titration and the analyst speaks of titrating the substance under investigation. The process is to place the standard solution in a burette, noticing the exact height of the liquid if it does not stand at the zero mark. From this the solution is allowed to slowly flow into the liquid that is being tested, stirring continually to cause immediate mixing. When enough of the reagent has been added to complete the reaction the amount is carefully read from the burette and the unknown quantity of the other substance is calculated. In order that a volumetric method of quantitative analysis should be exact it is necessary that the end reaction, or point when sufficient of the reagent is present, should be plainly visible through some change in the appearance. Sometimes this occurs spontaneously when the chemical change is complete but very often a third substance called an indicator must be added.

The calculation of the results may be made in a number of ways. It should be remembered that although the measurements are by volume the results are in terms of weight and that therefore volume should be converted into weight as soon as possible. Suppose that in the determination of the percentage of silver in an alloy with copper after dissolving one gramme of the alloy in nitric acid 5.0 cc. of the normal hydrochloric acid should be exactly suffi-

cient to precipitate the silver. Each cc. of the normal solution containing 0.03618 grm. of HCl, 0.1809 grm. of HCl would have been thus used. By the method of proportion given on page 255 we have

$$\begin{array}{ccccc} \text{Weight of HCl} & : & \text{Weight of Ag} & = & \\ 36.18 & : & 107.12 & = & \end{array}$$

$$\begin{array}{ccc} \text{Weight of HCl} & : & \text{Weight of Ag} \\ 0.1809 \text{ grm.} & : & 0.5356 \text{ grm.} \end{array}$$

or 53.56 per cent. of silver in the alloy.

Or again, as the equation above shows that each cubic centimeter of normal HCl precipitates 0.10712 grm. Ag, the amount of silver present can be obtained by multiplying this by the volume of the acid used. That is (since normal solutions contain $\frac{\text{molecular weight}}{1000}$ of univalent compounds, $\frac{\text{molecular weight}}{2000}$ of bivalent compounds, etc., and since one cubic centimeter of this normal solution acts upon $\frac{\text{molecular weight}}{1000}$ of other univalent compounds, $\frac{\text{molecular weight}}{2000}$ of other bivalent compounds, $\frac{\text{molecular weight}}{3000}$ of other trivalent compounds, etc.) in volumetric determinations *multiplication of the number of cubic centimeters of a normal solution necessary for a complete chemical reaction, by* $\frac{\textit{molecular weight}}{1000}$ *of a univalent compound, whose amount is being ascertained or by* $\frac{\textit{molecular weight}}{2000}$ *of bivalent compounds, etc., gives the weight of the latter iu grammes.*

CHAPTER II. ANALYSIS BY NEUTRALIZATION.

OF this there are two kinds, acidimetry — the determination of acids, or substances with an acid reaction — and alkalimetry — the determination of alkalies, or substances having an alkaline reaction. A standard alkali or acid is added from the burette to the solution of unknown strength until the reaction of the mixed solutions is neutral. This point is shown by the addition of an indicator. This is a substance which is of one color in liquids of alkaline reaction and another when the reaction is acid. A number of such are used in acidimetry and alkalimetry. In some instances one is to be preferred and in some another, so that there can be no such thing as the one best indicator for all cases. Some from their color, cannot be used with liquids of a certain shade; some have their sensitiveness lessened, or their action prevented, by ammonia, carbon dioxid, etc.; some are affected by mineral acids but not by organic acids, so that the selection of the proper indicator is a matter of importance. The properties of some of the most common are given in Table VII.

The Preparation and Properties of Standard Solutions.

These can be prepared either by standardizing by means of other standard solutions, when it is inconvenient or impossible to weigh the reagent which is to be dissolved, as in the case of gaseous reagents or those which contain an indefinite quantity of water. Or they may be made, as is most frequent, by weighing out the proper amount of the

TABLE VII.

INDICATORS FOR ACIDIMETRY AND ALKALIMETRY.

Name.	Color in Acid Solutions.	Color in Alkaline Solutions.	Advantages.	Objections and Interferences.	Remarks.
Litmus.	Red.	Blue.	Seen with sodium flame red appears colorless; blue becomes very dark.	CO_2 prevents sharp end-reaction; cannot well be used for carbonates. Unsatisfactory with phosphoric and many organic acids.	If used with carbonates the CO_2 must be expelled by boiling.
Phenolphthalein.	Colorless.	Reddish-pink.	Very sensitive, changing suddenly with reaction. Can be used with alcoholic solutions, also with many colored liquids. It is affected by both mineral and organic acids.	Inadvisable with carbonates (CO_2) or ammonia compounds. Useless with borax.	CO_2 can be expelled by boiling. With phosphoric acid it indicates neutrality when two hydrogen atoms are replaced by a metal.
Methyl orange.	Pink.	Faint-yellow.	Can be used with carbonates, sulphids and borates, also ammonium compounds.	Cannot be used with most organic acids. Change of color is indistinct by artificial yellow light.	With phosphoric acid indicates neutrality when one hydrogen atom is replaced by a metal. Only a few drops should be used.
Rosolic acid also called aurin and corallin.	Pale yellow.	Violet red.	Can be used with mineral acids and oxalic acid.	Is not reliable for other organic acids. Its sensibility is lessened by CO_2 or ammonium compounds.	
Cochineal.	Reddish-yellow.	Violet.	Can be used with ammonia and by gas light. CO_2 does not interfere. The change of color is well marked with the alkaline earths.	Traces of iron, aluminum compounds or acetates interfere.	
Lacmoid.	Red.	Blue.	Can be used for mineral acids alone or in presence of metallic salts, also with borates.	CO_2 interferes; cannot be used with carbonates except while boiling.	Many metallic salts like sulphates and chlorids of iron, zinc and copper are neutral to lacmoid though acid to litmus.

solid reagent, placing this in a measuring flask (usually one holding a liter) filling it to the mark with distilled water of a temperature of 15° and thoroughly mixing after solution has occurred. When not in use they should be preserved in tightly closed bottles. Some slowly change in strength for a long time after they have been prepared, and others are so unstable that special methods of preservation must be employed and their strength must be determined before each new series of analyses. Too great pains cannot be taken to insure correctness in the standard solutions.

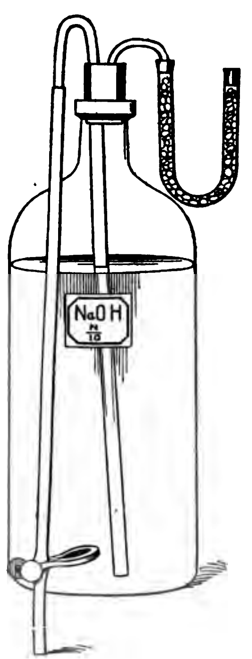
Standard Solutions for Acidimetry and Alkalimetry.

Normal Sodium Carbonate, Na_2CO_3.—Pure anhydrous sodium carbonate is to be heated to a low red heat and after cooling, 52.59 grms. are dissolved in pure water and the volume made up to one liter. If the pure salt is not at hand 85 grammes of sodium bicarbonate which is usually easily obtained in the pure state, will, by heating to drive off the water and carbon dioxid, give rather more than this weight of the pure carbonate.

Normal Sodium Hydrate, $NaOH$.—This contains in one liter 39.70 grams of pure NaOH. Since the solid substance as purchased contains a varying amount of moisture and consequently cannot be accurately weighed, the solution should be made at first stronger than is required, its strength ascertained, and should then be diluted with the calculated volume of water. As both the solid and the solution unite with carbon dioxid care must be taken to prevent its access to them. Put about 45 grammes of pure, dry sodium hydrate into a liter flask and fill to the mark with cold distilled water from which the carbon dioxid has been lately expelled by boiling. After dissolving and thoroughly mixing remove 10 cc. by a pipette to a small beaker and add a few drops of phenolphthalein solution. From

a burette run in normal hydrochloric acid until, after stirring, the liquid becomes permanently a faint pink. Repeat this several times and if the determinations nearly agree take their average; calculate the strength of the alkaline solution and the amount by which it must be diluted to make it normal. If, for example, 11 cc. of the normal acid is necessary to neutralize 10 cc. of the sodium hydrate where if the latter were normal only 10 cc. of acid would be required, the alkali is stronger than normal. Enough water must be added to dilute each 10 cc. of the hydrate to 11 cc.—that is, the one tenth of its bulk. For example if 50 cc. of the liter first prepared have been used in the preliminary testing 95 cc. of water should be added to the remainder (in a larger flask, since this makes more than a liter). If the determination was correct 10 cc. of this solution will now exactly neutralize 10 cc. of the normal acid. For preservation the solution should be kept in a bottle having a two-holed rubber stopper. Through one hole passes a syphon tube with a rubber tube and spring clamp on the end; to the other is attached a tube filled with small fragments of soda-lime. The air can pass through this but its carbon dioxid is absorbed. It is sometimes recommended that this soda-lime tube be vertical but it will be found that after a long time enough moisture will be attracted from

FIG. 16.



Bottle for the preservation of standard solutions which are affected by the carbon dioxid of the air.

the air to liquefy the soda-lime and this, being itself alkaline, by running into the standard solution will alter its alkalinity. A U-tube does not involve this danger. Other standard alkaline solutions, ammonium, potassium or barium hydrate, etc., can be prepared in a similar manner.

Normal hydrochloric acid, HCl, contains 36.18 grms. in a liter. Since the acid as purchased is of variable strength the normal acid must be made by standardizing by means of a standard alkaline solution. Dilute about 130 cc. of the concentrated hydrochloric acid (specific gravity 1.16) to a liter, which will make it above normal strength. Mix well and remove 10 cc. to a small beaker, adding a few drops of methyl-orange solution. From a burette allow a normal sodium carbonate solution to flow slowly in, stirring meanwhile, until the color of the liquid changes from a pink to a pale yellow. Take the average of several determinations and calculate the amount by which it must be diluted to make 10 cc. of one solution neutralize 10 cc. of the other. Add this and test it to make sure that it is correct. Thus if 10 cc. of the acid requires 12.5 cc. of the normal carbonate to neutralize it, for each 10 cc. of the acid 2.5 cc. of water must be added.

Normal oxalic acid, $H_2C_2O_4,2H_2O$ contains 62.55 grms. of the crystallized solid per liter. The solution may be prepared by weighing out this amount if the crystals are bright in appearance and free from moisture. They are, however, very efflorescent, losing a great part of their water of crystallization when exposed to the air, then becoming dull in appearance, and should not be used for making the solution by weight.' The pure crystals leave no residue if they are ignited on platinum foil. If such a residue remains it is a sign of an impurity. If the pure crystals cannot be obtained a slightly greater weight than given above may be taken (perhaps 65 grammes), and, after

dissolving in water in a liter flask and diluting to a liter, the strength may be learned by titrating with the normal sodium hydrate, using phenolphthalein for the indicator. This solution will be too strong and should be reduced by adding the calculated amount of water as in the preparation of normal hydrochloric acid. The solution decomposes in direct sunlight. Very dilute solutions do the same in weak light so that if decinormal or centinormal solutions are needed the normal solution should only be diluted with water shortly before it is to be made use of.

Other acids, sulphuric, tartaric, etc., can be standardized by a similar course of procedure.

Acidimetry.

For the standard solution normal sodium carbonate or sodium hydrate may be used. Place this in the burette, making a note of its height if it is not at the zero mark, and with a pipette carefully measure a definite volume, perhaps 10 cc. of the liquid of which the acidity is to be determined, transferring it to a small beaker. To this add a few drops of the indicator, selected in accordance with Table VII. For the titration let the standard alkali flow slowly into the acid, stirring meanwhile in order to thoroughly mix the two liquids. At first the color, produced when the alkali meets the indicator, vanishes immediately. When it disappears only slowly the normal solution should be added by drops so as to avoid an excess, stopping when the change in color of the indicator is persistent throughout the liquid. The amount drawn from the burette should be ascertained and noted and the titration repeated. It is best to take the average of several nearly concordant results than to depend upon one. Knowing the weight of each acid which will be neutralized by one cubic centimeter, the weight present in the volume

used can be calculated. The final results can be expressed as grammes per liter or in percentage by weight. In a liter of water there are 1,000 grammes (cc.) and consequently if the liquid being tested is of the same specific gravity as water the percentage by weight (that is, parts in a hundred) can be obtained from the grammes per liter by dividing by ten. When the specific gravity is greater or less than one the result so obtained must be divided by the specific gravity to find percentage. It is to be understood, of course, that acids combined in neutral salts cannot be determined in this manner.

Practical Exercises in Acidimetry.

1. Determine the strength of dilute sulphuric and nitric acids furnished by the instructors, reporting results. Use normal sodium carbonate, with methyl orange for an indicator.[1]

2. From concentrated hydrochloric acid prepare a normal solution according to the directions on page 169.

3. After the preparation of normal sodium hydrate (page 167) standardize a normal solution of oxalic acid (page 169).

Other chemical compounds which have an acid reaction can be determined quantitatively by similar methods after the choice of a suitable indicator. Among those with which sodium hydrate and phenolphthalein can be used are acetic acid (vinegar), lactic acid (sour milk) or acidity of gastric contents (with $\frac{N}{10}$ NaOH), aromatic sulphuric acid, hydrobromic acid, and hypophosphorous acid, HPH_2O_2, (univalent, the equation being

$$NaOH + HPH_2O_2 = NaPH_2O_2 + H_2O).$$

[1] In the practical exercises a single titration ought not to be depended upon but the average of two or three closely agreeing ones should be taken.

In all cases the basicity of the acid must be considered, as this determines the amount of alkali necessary to neutralize the molecule.

Alkalimetry.

In this the operations of acidimetry are reversed, the standard acid solution being placed in the burette and the alkaline solution below. Otherwise the method is as before. In addition to its use in determining the amount present of a substance with an alkaline reaction it can be used for the same purpose with another class of compounds — that is, the salts of organic acids which have as a base one of the alkali metals. These when ignited are changed into carbonates of those metals. The carbonates are alkaline in reaction although the salts from which they are derived may be acid or neutral. One molecule of the carbonate requires for its formation a sufficient number of molecules of the organic compound to furnish two atoms of the metal. Thus one molecule of a normal tartrate gives one molecule of carbonate,

$$K_2C_4H_4O_6 + 5O = K_2CO_3 + 2H_2O + 3CO_2.$$

Two molecules of an acetate or acid tartrate form the same amount.

$$2KC_2H_3O_2 + 4O_2 = K_2CO_3 + 3CO_2 + 3H_2O.$$
$$2HKC_4H_4O_6 + 5O_2 = K_2CO_3 + 7CO_2 + 5H_2O.$$

Two molecules of a normal citrate form three of a carbonate,

$$2K_3C_6H_5O_7 + 9O_2 = 3K_2CO_3 + 9CO_2 + 5H_2O.$$

It will not be necessary to burn off all the carbon to form the carbonate — that is to heat long enough to leave a perfectly white residue. If the organic salt is at first in solution a measured amount must be evaporated to dryness, then the solid must be heated in a platinum or porcelain crucible,

gently at first, to avoid loss, then until the mass is completely carbonized, which will require a red heat. If the compound is a solid, a weighed quantity (one to two grammes) should be treated in the same way. After cooling the carbonate will dissolve easily in hot water. It should be filtered and the carbon washed with small amounts of hot water until it is no longer alkaline. The weight of carbonate can be determined by titration and, knowing the number of molecules of the organic salt from which one of the carbonate is derived together with their relative molecular weights, the weight of the original salt is readily calculated.

Practical Exercises in Alkalimetry.

1. Using normal hydrochloric acid for the standard determine the strength of an unknown solution of ammonium hydrate with cochineal or rosolic acid as indicator; of borax with lacmoid as an indicator.

2. Prepare a normal solution of sodium hydrate by the method outlined on page 167.

3. Ignite thoroughly in a platinum or porcelain capsule a weighed amount of acid potassium tartrate, extract with hot water, titrate the filtrate, using normal hydrochloric acid and methyl orange, and from calculated result form an opinion as to the purity of the tartrate.

4. Evaporate to dryness in a porcelain capsule 10 cc. of a strong solution of sodium acetate, ignite, titrate the soluble part and calculate the strength of the solution.

Among the other compounds of which the amounts can be found by alkalimetry are the hydrates and carbonates of the alkali metals, the hydrates of the alkaline earths, the tartrates of sodium and potassium, the acetate of potassium, the citrates of potassium and lithium, the benzoates of lithium and sodium, and the salicylates of lithium and sodium.

CHAPTER III. ANALYSIS BY OXIDATION (OR OXIDIMETRY), AND BY REDUCTION.

THE method is based upon the fact that certain compounds have the power of oxidizing definite amounts of other compounds when in solution. In some cases the end of the reaction is indicated by a change in the color of the standard; in others indicators are added. The results obtained are very accurate. The most common oxidizing agents used for the standard solutions are potassium permanganate, $KMnO_4$; potassium dichromate, $K_2Cr_2O_7$, and iodin.

The Preparation and Properties of Standard Oxidizing Solutions.

Potassium permanganate, $KMnO_4$, can be obtained pure in the crystalline form, though it is so often impure that the strength of the solution should be tested after making by titrating against a standard. The crystals dissolve to an intensely reddish-purple solution. The molecular weight of the substance is 156.97. As stated before (page 162) when it acts as an oxidizing agent two molecules yield five atoms of oxygen. The combined valences of the five atoms of oxygen given by this double molecule is ten. Therefore a normal solution would contain one-tenth the double molecular weight of the salt in a liter or 31.39 grammes. The decinormal solution containing 3.139 is more commonly employed. This solution is likely to undergo slight decomposition on standing, although it will maintain its strength for several weeks. Unless freshly prepared it should be standardized before the solution is used, in the same

manner as in the original preparation. Organic matter produces changes in the solution which should therefore not be brought into contact with rubber. A pouring burette or one with a glass stop-cock is suitable for its measurement. When the permanganate gives up its oxygen, providing a free mineral acid is present, the purple color disappears as a result of the formation of the colorless manganese salt of the acid. This decolorization indicates the completion of the reaction. An indicator is therefore unnecessary. If the crystals are known to be pure the weighed amount can be dissolved in a liter of water. In case of doubt as to their purity about 3.5 grammes should be so dissolved, the strength of the solution ascertained by one of the following methods and the proper volume of water added to reduce it to its desired strength.

The substances most commonly used to ascertain the strength of a permanganate solution are oxalic acid, ammonium ferrous sulphate, and metallic iron.

A decinormal solution of oxalic acid can be taken as the standard. The reaction is

$$\begin{aligned} 2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \\ = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O. \end{aligned}$$

The 10 cc. of the oxalic acid is measured with a pipette and after acidifying with dilute sulphuric acid, is placed in a flask or beaker and the mixture warmed to about 60°. Then the permanganate solution is allowed to run in. At first the color disappears slowly but afterwards more rapidly. If it turns brown the amount of sulphuric acid is insufficient. The permanganate should be added cautiously to avoid an excess, stopping when the pink color is permanent. From the average of several determinations calculate the strength of the permanganate solution, remembering

that if it were decinormal exactly 10 cc. would be reduced by the oxalic acid. Find the volume of water which will, if added, produce the decinormal solution, as in the preparation of standard solutions of sodium hydrate (page 167) or hydrochloric acid (page 169). After dilution test again to see if the strength is correct. It is well in this second test to make use of another standard solution such as one of decinormal ferrous ammonium sulphate.

Ferrous ammonium sulphate, $(NH_4)_2Fe(SO_4)_2$, $6H_2O$, can be obtained pure in the form of greenish crystals. For this purpose they must not have lost any of their water by efflorescence or be at all brown in color, which indicates that the iron is changing to the ferric form. A decinormal solution containing 38.34 grams to the liter should be used with sulphuric acid in the same manner as in the titration by oxalic acid. The reaction is

$$10(NH_4)_2Fe(SO_4)_2 6H_2O + 2KMnO_4 + 8H_2SO_4 = K_2SO_4 \\ + 10(NH_4)_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 14H_2O.$$

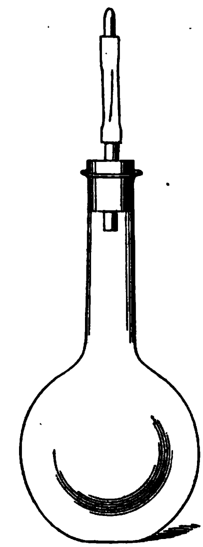
Here as before one cubic centimeter of the iron solution should decolorize exactly one of the decinormal potassium permanganate.

If metallic iron is the standard about 0.1 grm. of the purest piano wire, accurately weighed, should be dissolved in a flask by means of dilute sulphuric acid. Access of air can be prevented by a Bunsen valve made of a short piece of slit rubber tubing slipped over the exit tube and closed at the upper end, which allows the hydrogen to escape. When the wire has dissolved, the solution can be diluted with recently boiled water and immediately titrated with the permanganate. The reaction is similar to that with the ammonium ferrous sulphate because the iron in dissolving forms ferrous sulphate, $FeSO_4$. Since all iron contains carbon allowance must be made for this. If it

has not been determined in the sample which was used, the wire may be estimated at 99.6 per cent. pure.

Of *iodin* the decinormal solution is used. This contains 12.59 grms, in the liter. It can be made by dissolving about 18 grms. of pure potassium iodid in 200–300 cc. of water in a liter flask, adding 12.59 grms. of chemically pure iodin and when this has dissolved, filling to the mark with water. If pure iodin cannot be obtained somewhat more than this amount may be dissolved and the strength of the solution be ascertained by titrating with a standard solution of sodium thiosulphate (hyposulphite) in the manner described below. The iodin solution should be kept in a cool, dark place, but even then it does not maintain its strength, so that unless it has been recently prepared it should be standardized before using.

FIG. 17.



Flask fitted with Bunsen valve which allows the gas to escape from within but prevents the access of air.

The oxidizing action of the iodin is an indirect one. It unites with the hydrogen of the water present, leaving the oxygen free to combine with oxidizable substances. This is illustrated by its action on sodium sulphite or arsenous oxid.

$$Na_2SO_3 + I_2 + H_2O = 2HI + Na_2SO_4.$$
$$As_2O_3 + 2I_2 + 2H_2O = 4HI + As_2O_5.$$

Although solutions of free iodin have a color and most solutions of its compounds do not, the distinction is not great enough to accurately mark the end reaction. Therefore a few drops of a boiled starch solution are added as an indicator. This gives a deep blue color as long as any

free iodin is present and is colorless when the iodin is in combination with other elements.

Decinormal potassium dichromate, $K_2Cr_2O_7$, which is often used in oxidimetry, contains 4.87 grms. in a liter. The crystallized salt can be obtained in a pure state and the solution may be made by drying the salt at 100°, then dissolving this weight in water and diluting to a liter. The solution is much more permanent than that of potassium permanganate or iodin and is not affected by contact with rubber. An indicator must be used with it in the volumetric tests of ferrous compounds and this lessens its convenience. When the dichromate is used as an oxidizing agent it loses three atoms of oxygen. It is for this reason that its decinormal solution contains one sixtieth of its molecular weight in grammes per liter (page 162). The sulphuric acid combines with the potassium and chromium forming the sulphates of these metals. Thus

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + O_3.$$

The principal use of the dichromate solution in volumetric analysis is in the quantitative determination of iron and its ferrous compounds. If a ferrous compound is present with an acid the oxygen unites with the hydrogen of the latter, and the acid radical combines with the iron, changing it to the ferric state.

$$6FeSO_4 + 3H_2SO_4 + O_3 = 3H_2O + 3Fe_2(SO_4)_3.$$

Analysis by Reduction.

This is the opposite of oxidimetry. Soluble reducing agents, or deoxidizers will remove oxygen from many of its compounds when in solution and if the end of this reducing action is definitely marked they may often be employed in the preparation of standard volumetric solutions. Oxalic acid and sodium thiosulphate are very commonly used. The former has already been discussed.

Sodium thiosulphate, $Na_2S_2O_3, 5H_2O$, contains in a liter of the decinormal solution 24.63 grms. of the crystallized salt. The solution can be prepared by dissolving in water this weight of the pure crystals which have been dried by pressing in blotting paper after pulverizing, then diluting to a liter. The solution should be kept in the dark. It even then decomposes slowly, however, so that old solutions can not be depended upon. Sodium thiosulphate is principally used in volumetric analysis in the determination of free iodin. This includes the determination of other substances like bromin and chlorin, one atom of either of which sets free one atom of iodin from an iodid. If, therefore, to a solution of free bromin or chlorin a little potassium iodid is added, the bromin or chlorin frees the iodin. The amount of iodin indicates that of bromin or chlorin.

Practical Exercises in Analysis by Oxidation and Reduction.

1. From the normal solution of oxalic acid previously prepared make a decinormal solution by diluting one volume with nine of water. By the aid of this standardize a decinormal solution of potassium permanganate by the method described on page 174.

2. With the decinormal permanganate make a determination of the amount of iron in a solution of ferrous sulphate, calculating the weight of Fe and $FeSO_4$ present.

3. By the aid of a decinormal solution of potassium dichromate (made by the directions given) make a titration of the same ferrous solution. Determine the end of the reaction by removing a small drop of the solution on the end of a glass rod and with this stirring a drop of a dilute, freshly prepared solution of potassium ferricyanid as an indicator. As long as there remains any of the unoxidized iron a blue color will result. When a sufficient dichromate is present only a brownish-yellow appears.

The tests are most conveniently made by placing a number of drops of the indicator on a porcelain plate and touching these with the stirring rod after the addition of each portion of the dichromate. The results obtained by this method should agree with those by the permanganate. They thus serve to confirm the correctness of the dichromate solution as well as of the accuracy of the determination of the amount of iron.

4. Use the decinormal permanganate to determine the strength of a solution of hydrogen peroxid (dioxid). The reaction is $5H_2O_2+2KMnO_4+3H_2SO_4=K_2SO_4+2MnSO_4+8H_2O+5O_2$. Measure into a beaker one cubic centimeter of the peroxid by means of a pipette and dilute with 10 to 20 times its volume of water acidified with H_2SO_4. From a burette add the permanganate slowly until there is a permanent pink color. (In the U. S. P. process 10 cc. of the peroxid are diluted to 100 cc., and 17 cc. of this is titrated. The Pharmacopœia requires it to decolorize 30 cc. of the decinormal permanganate. This corresponds to a 3 per cent. solution by weight.) Calculate the percentage strength of the hydrogen peroxid solution by weight.

Instead of being expressed by weight the strength of the hydrogen peroxid is more often referred to the volume of oxygen which it will evolve when decomposed by heating. One atom is thus set free from each molecule, or one-half the amount that is given off when it is acted upon by potassium permanganate, as represented by the above equation. For each two molecules of the permanganate which are decolorized, therefore, there are present five atoms of active oxygen in the peroxid. Consequently one cc. of the decinormal permanganate corresponds to 0.0008 grm. of such active oxygen. From the results obtained in the above determination of the strength of hydrogen peroxid by weight calculate its oxygen volume of active oxygen,

using 0.00143 grm. as the weight of one cubic centimeter of oxygen.

5. Iron is determined quantitatively by permanganate or dichromate solutions, but only when it is in the ferrous form. Hence ferric compounds must be reduced to ferrous before they are titrated. This can be effected by a number of reducing agents. Place in a flask fitted with a valve as described above (page 177) 10 cc. of a ferric solution, acidify with sulphuric acid and add a few small fragments of granulated zinc which is free from iron or in which the amount of iron is known (using then a definite weight of zinc). Let it dissolve completely when, if the iron is reduced, the liquid will be colorless with no yellow tint. Then titrate immediately with the decinormal permanganate solution and, after the amount of iron has been found, calculate the weight and percentage of the ferric compound in the original solution.

6. With the aid of a decinormal solution of sodium thiosulphate determine the strength of a solution of iodin, as follows: Into a measured volume of the iodin solution run, from a burette, the standard thiosulphate until the brown color has almost disappeared. Then add a few drops of a starch solution and continue the titration until the blue is just destroyed, leaving the liquid colorless. The reaction is then completed, the thiosulphate being converted into a sodium tetrathionate,

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

7. Chlorin or bromin when brought into contact with potassium iodid liberates an equal number of atoms. In consequence of this action the strength of chlorin or bromin water is easily found. To 10 cc. of the solution add about half a gramme of potassium iodid in crystals or solution and titrate with starch as an indicator, as in the last operation.

8. In the same manner determine the amount of the calcium hypochlorite, $CaOCl_2$, or sodium hypochlorite, NaOCl, or potassium hypochlorite, KOCl, from which the available chlorin is set free by acids.

$$CaOCl_2 + 2HCl = CaCl_2 + H_2O + Cl_2.$$

$$2NaOCl + H_2SO_4 = Na_2SO_4 + H_2O + Cl_2.$$

Acidify a known volume with hydrochloric acid and after the addition of potassium iodid and starch, titrate with the thiosulphate as in the preceding exercises.

The presence of chlorates lessens the accuracy of the last determinations.

9. With starch as an indicator compare the strength of the decinormal thiosulphate (page 179) with the decinormal iodin solution (page 177) to prove that both are correct.

10. When a ferric salt is warmed with potassium iodid it is changed to the ferrous state, one atom of iodin being set free for each atom of iron.

$$FeCl_3 + KI = FeCl_2 + KCl + I.$$

The quantitative method of determining ferric compounds based upon this reaction is carried out in the following manner.

To 10 cc. of the ferric solution add about a gramme of potassium iodid and 2 cc. of hydrochloric acid. By the above reaction the iodid is slowly set free. The mixture should be placed in a 100-cc. glass-stoppered bottle and the whole warmed in water two hours at 40°. The temperature should not be allowed to exceed this nor the stopper be removed because of danger of loss of iodin through volatilization. Cool, and after the addition of a few drops of starch solution, titrate with decinormal sodium thiosulphate. Calculate the amount of the ferric salt, reckoning one atom of iron for each one of free iodin.

11. Prepare a decinormal solution of iodin by weighing (page 177) or take a larger amount than is necessary, dissolve in the same manner, determine its strength by titration and dilute to the standard.

12. With the standard iodin solution make a determination of a solution of arsenous acid, H_3AsO_3, or an arsenite, like potassium arsenite, K_3AsO_3. In the case of the arsenous acid pure sodium or potassium bicarbonate must be present to neutralize the hydriodic acid formed in the titration. Five to ten times as much of this should be used as the estimated weight of the arsenous acid. The titration is carried out as before until the starch indicator is colored a faint blue. A gentle heat may be used to aid in the solution of the bicarbonate but it cannot be heated high enough to decompose the bicarbonate as the carbonate thus produced would interfere with the action of the indicator. If a free alkali other than a bicarbonate is present it must be neutralized by hydrochloric acid and any acids must be neutralized with a bicarbonate before titration. The reaction between the iodin and arsenite is similar to that with the arsenous oxid already referred to.

$$2K_3AsO_3 + 2I_2 + 2H_2O = 2K_3AsO_4 + 4HI.$$

CHAPTER IV. ANALYSIS BY PRECIPITATION.

HERE the standard solution converts the compound of which the amount is sought, or some constituent of it into an insoluble form, thus producing a precipitate. Knowing the amount of the standard necessary to effect this result the weight of the precipitate or of the substance from which it is derived can be calculated. As the point where precipitation is complete is, in almost all cases, indistinct, indicators are usually required in this class of analysis. These are such compounds as will not be acted upon by the standard until the compound under investigation has been completely transformed and which will then react with the excess of the standard solution producing a color or some other visible change.

Precipitation is also often used in combination with other methods of volumetric determination. Thus soluble compounds of barium, strontium and calcium can be precipitated as neutral carbonates by ammonia and ammonium carbonate. If these precipitates are washed and suspended in water they can be titrated by solutions of the normal acids, their amount being calculated from the volume of acid necessary to produce an acid reaction. The equations representing the chemical change occurring during their solution may be represented by the following:

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

The Preparation and Properties of Standard Solutions Used in Analysis by Precipitation.

Decinormal Silver Nitrate, $AgNO_3$. — As the crystals can usually be obtained in the pure state this can be made

by dissolving 16.87 grms. in sufficient water to make the volume of the solution one liter. Or a somewhat greater weight may be dissolved, if the purity is doubtful, and the strength ascertained by titration against decinormal sodium chlorid. Instead of the sodium chlorid decinormal hydrochloric acid can be used. In the latter case after the amount to be used has been accurately measured by a pipette it must be carefully neutralized with sodium carbonate before the titration, avoiding an excess of the carbonate. The value of the silver nitrate in analysis by precipitation is that it forms insoluble compounds with the chlorids, bromids, iodids and cyanids. The indicator is generally normal (yellow) potassium chromate. This forms an insoluble, dark-red, silver chromate with the silver nitrate, but not until the above-mentioned compounds have been precipitated, if they are present in the solution. The end reaction is most clearly seen if instead of daylight a yellow light, like that of gas, is used, the titration being conducted in a rather dark place.

The silver nitrate solution is decomposed by the action of light and by organic matter. It should therefore be preserved in an amber-colored bottle or in a dark place. It should be protected from dust and not be used in burettes which have rubber-tubing connections.

Decinormal Potassium Sulphocyanate, *KSCN*, contains in a liter 9.65 grms. of the salt. It cannot well be prepared by weighing the solid, since it is deliquescent. About 10 grammes of this should be dissolved in a liter of water and 10 cc. of decinormal silver nitrate titrated with the solution after acidifying with 5 cc. of dilute nitric acid. The reaction is shown by the following equation:

$$AgNO_3 + KSCN = AgSCN + KNO_3.$$

About ten drops of a solution of ammonium ferric sul-

phate (iron alum) is to be added for an indicator. The silver sulphocyanate is precipitated first, giving the liquid a milky appearance. When all the silver has been converted into this compound the sulphocyanate acts on the indicator producing red ferric sulphocyanate which indicates the end reaction. With a solution prepared in this way less than 10 cc. of the sulphocyanate should at first precipitate 10 cc. of the decinormal silver nitrate. The amount of water which must be added to dilute it to a strength corresponding to that of the silver solution can be calculated as in the preparation of standard solutions of sodium hydrate and hydrochloric acid. When this has been added it should be tested again in the same manner to ascertain its correctness. This sulphocyanate solution may be used for the estimation of silver, even in the presence of many other dissolved metals, since most of these are unaffected by the reagent. It can also be employed in connection with decinormal silver nitrate to determine the amount of any substance which is completely precipitated by the latter compound. This includes all those mentioned as capable of being determined by standard silver nitrate. In this case the method is that of *residual titration*. It consists in adding to the solution a measured quantity of the decinormal silver nitrate, greater than is sufficient to precipitate the compound, then titrating this with sulphocyanate to learn what the excess is. The difference in cubic centimeters between the volumes of silver nitrate used and sulphocyanate used shows the amount of standard silver solution which is taken up by the substance under investigation. From this its weight is obtained. The end reaction is rather easier to distinguish than when potassium chromate is the indicator.

The standard solutions of silver nitrate and potassium sulphocyanate may be employed in the estimation of any

compounds of the metals which can be converted easily and without loss into chlorids. This can be done with the carbonates, hydrates, oxids and nitrates of potassium, sodium, ammonium, calcium, strontium, barium, magnesium and some other metals, by the action of hydrochloric acid; also with the chlorates, which by ignition set free oxygen and are changed to chlorids. Carbonates may be decomposed with the evolution of carbon dioxid and nitrates with a setting free of nitric acid. This is accomplished by adding to a weighed or measured amount of the substance under investigation an excess of the acid (after evaporation to dryness in case of solutions) using the concentrated acid with nitrates. The excess of the acid, that is the part which has not united with the metal to form chlorids, must be completely driven off by first evaporating to dryness on a steam-bath, then heating in an air-bath at 120° until a piece of blue litmus paper laid across the dish is no longer reddened. The chlorid is then dissolved in water and this solution titrated as before, using a known fraction of the liquid and making duplicate determinations. After the determination of the chlorin the weight of the metal, and hence the original compound, can be calculated.

Practical Exercises in Analysis by Precipitation.

1. Prepare decinormal silver nitrate by one of the methods given above.

2. With this solution determine the percentage strength of a solution of sodium chlorid. Use only enough of the potassium chromate to make the solution slightly yellow, which will take but a few drops. With a larger quantity it becomes more difficult to tell when the silver chromate commences to be permanent. Make the titration by yellow light or gas light if convenient (not that of an incan-

descent burner, however). One molecule of silver nitrate precipitates one of the chlorid.

$$AgNO_3 + NaCl = AgCl + NaNO_3.$$

3. In the same manner determine the strength of a solution of potassium bromid.

4. Potassium cyanid upon the addition of silver nitrate forms at first no precipitate but the soluble double cyanid, KCN, AgCN.

$$AgNO_3 + 2KCN = KCN, AgCN + KNO_3.$$

When, by this means, all the potassium cyanid has been thus changed any excess of silver nitrate decomposes the double salt and a precipitate appears. This reaction can be made use of as a quantitative method. Into 10 cc. of the potassium cyanid solution run from the burette decinormal silver nitrate, stirring continually. The equation above shows that as soon as a permanent precipitate appears, for each molecule of the silver nitrate used two of the cyanid have entered into reaction. 1 cc. of decinormal silver nitrate accordingly corresponds here to 0.0129 grm. of potassium cyanid, that is, twice as much as in corresponding reactions between other salts and silver nitrate, because of the formation of the double salt. In this method no indicator is necessary. Ascertain by it the percentage strength of a solution of the cyanid.

5. With hydrocyanic acid silver nitrate gives the following reaction:

$$AgNO_3 + HCN = AgCN + HNO_3.$$

The nitric acid thus formed would interfere with the titration and must be neutralized. This can be done by stirring into the hydrocyanic acid that is to be titrated, after measuring, enough of an aqueous suspension of magnesia to give an alkaline, milky mixture. Then add a few drops

of potassium chromate and the standard silver nitrate until the red silver chromate does not disappear after stirring. Avoid inhaling the vapor of hydrocyanic acid! It should not be drawn into the pipette with the mouth. It is better to weigh the original portion than to attempt to measure it.

6. Prepare a decinormal solution of potassium sulphocyanate after the method outlined above (p. 185).

With the standard solutions of silver nitrate and sulphocyanate ascertain the strength of a solution of ammonium chlorid by the method of residual titration. To 10 c.c. of the chlorid solution add 5 cc. of the ammonium ferric sulphate indicator and 5 cc. of dilute nitric acid. From a burette run in a few drops of decinormal potassium sulphocyanate, then, from another burette, enough decinormal silver nitrate to make the color of the liquid a pure white. If sufficient has been used another addition of the sulphocyanate will give no red color. If it does, continue adding the silver solution until this condition is attained. The chlorin is then all precipitated as well as the whole of the sulphocyanate and there is present an excess of silver nitrate. Now allow the sulphocyanate solution to flow in slowly from the burette with constant stirring until the red color, which disappears at first, is permanent. This indicates that both the chlorid and sulphocyanate are exactly precipitated. The difference between the volumes of silver nitrate and potassium sulphocyanate used gives the amount of decinormal silver solution which was required to precipitate the chlorin. From this the weight of the latter can be calculated. This is known as Volhard's method.

7. Determine the strength of a calcium chlorid solution by making it alkaline with ammonium hydrate, then adding ammonium carbonate as long as precipitation occurs and heating to boiling for a few minutes. Filter and wash with hot water until the wash-water is no longer alkaline.

Then place the precipitate with the paper in a beaker with a small quantity of water. With methyl-orange as an indicator, titrate the liquid with normal hydrochloric acid until it changes to a permanent pink (acid) color. Calculate the percentage of the calcium salt in solution.

8. Mercuric chlorid when poured into a solution of potassium iodid forms a red precipitate (97). This dissolves, as it is stirred, as long as no more than one molecule of mercuric chlorid is present for four of potassium iodid. When there is more than this the red precipitate is permanent. The mercuric solution must be poured into the iodid and not the opposite. By this means the metal or any mercury compound can be quantitatively determined provided it can be first converted into mercuric chlorid. A decinormal solution of potassium iodid, made by dissolving the weighed crystals in water, may be used as the standard and one-fourth the molecular weight of mercuric chlorid reckoned as present for each molecule of the iodid necessary to obtain the permanent precipitate.

9. Make a determination of the amount of ammonium nitrate in a solution of this salt which also contains ammonium sulphate, using the method given above (page 187) of converting the nitrate into a chlorid.

10. Neutral soluble salts of which the bases can be completely precipitated by sodium carbonate can also be estimated by the use of a standard solution of the latter, the reaction being of the following type.

$$BaCl_2 + Na_2CO_3 = BaCO_3 + 2NaCl,$$

both the barium carbonate and sodium chlorid resulting being neutral. When the reaction of the liquid changes to alkaline it indicates that the barium has been precipitated. Salts of barium, strontium and calcium can be quantitatively determined thus. To ensure the certainty that they are fully precipitated the liquid must be heated to boiling.

Find the strength of a solution of barium nitrate, $Ba(NO_3)_2$, by first making it exactly neutral, then, after the addition of a few drops of phenolphthalein solution, titrating with normal sodium carbonate while the barium solution is at the boiling point.

Questions for Further Study in Volumetric Analysis.

What is the relation of the cubic centimeter to the gramme? Of the gramme to the liter? How many grammes in a liter of water? Is this the same for all liquids? What is the best method of preparing standard solutions from very hygroscopic or efflorescent compounds? What are some of the most commonly used reagents of these classes? If a compound containing water of crystallization is to be weighed to make up such a solution how can it be determined whether the theoretical amount of water is present or not? What would be the best method for preparing a standard solution of ammonium hydrate? Since both the standard sodium hydrate and sodium carbonate have an alkaline reaction and will neutralize acids why is it important to prevent the conversion of the former to the latter by carbon dioxid? Why cannot standard acids like hydrochloric, sulphuric and nitric be prepared by accurately weighing the pure concentrated acid and diluting this with a known weight of water? Which ones of the common standard solutions are stable, retaining their strength, and which must be standardized at each time of using? What is the nature of the blue compound formed by starch and iodin and what would be the effect of heating the liquid which contains it? Do standard solutions of reducing agents keep their strength permanently or not? Why? Are those of oxidizing agents more or less permanent? Under what conditions are both best preserved? Why is ferrous ammonium sulphate selected for

the standard solution of iron instead of crystallized ferrous sulphate? Given 10 grammes of dry, pure, sodium carbonate and the necessary measuring flasks, pipettes, etc., how can decinormal solutions of silver nitrate be prepared without further use of the balance? of potassium permanganate? of sodium hydrate? Starting in the same manner from 10 grammes of pure crystallized oxalic acid how is it possible to prepare standard solutions of hydrochloric acid? of ferrous sulphate? of silver nitrate?

PART III.

APPLIED ANALYSIS.

CHAPTER I. THE SANITARY EXAMINATION OF WATER.

ALL natural waters, whether known as well, spring, river or cistern water, have been precipitated to the earth as rain and before they can be used have been brought into contact with so many soluble substances that they are never chemically pure. The purest form is rain water, but this contains in solution the gases of the atmosphere and often in addition small particles which floated in the air in the form of dust. If it has passed through or over the soil it contains more or less of the mineral, vegetable or animal compounds with which it has been in contact. The dissolved gases are in general harmless and usually improve the taste of the water which without them is said to be flat or insipid. Of the other two classes of impurities—the mineral and organic—the mineral are by far the less objectionable. Unless they are present in large quantities they produce little physiological effect. If the amount is sufficiently great to affect the system the water is classed with the mineral waters which are so often used on account of their therapeutic value. Calcium and magnesium salts (principally the carbonate and sulphate) give to water the property commonly called "hardness," that is, it does not dissolve soap, and consequently does not have the soft feeling that is characteristic of soapy water. It is also im-

possible to produce a permanent foam or lather with such hard water by shaking it with soap solution unless a large amount of the latter is added. Considerable quantities of mineral matters are objectionable where the water is to be used for making steam as it sometimes deposits as "boiler scale" and sometimes attacks the iron of the boiler. Compounds of lead, copper or zinc should condemn a water since they are poisonous, but they are rarely found in it. Sodium chlorid is a valuable indication of the pollution of water. It is found in soils where this has not occurred but then, as a rule, only in very small quantities. The normal amount in any locality can be determined by testing the water from a number of sources in the region, this being practically a constant. As salt is always present abundantly in animal excreta and as it is soluble it will be taken up by any water that may come in contact with it.

Organic matter, vegetable or animal, in water, may be considered dangerous, and when abundant should forbid its use for drinking. Unfortunately the term organic matter does not mean one chemical compound but rather a complex mixture of varying nature so that its identification is often a matter of some difficulty. This is especially true of the distinction between vegetable and animal substances, which are composed of the same elements and contain similar compounds. They, therefore, respond to the same test in many cases. They are, moreover, when contained in water, in a state of decomposition, becoming converted into other compounds. Thus the nitrogen, which is one of the characteristic elements of this mixed organic matter, appears after bacterial disintegration, first in ammonia, then it nitrites and lastly in nitrates. Since neither of the three last are found in soil or air, except in traces, these may be assumed to indicate that the water contains, or has at some time contained, vegetable or animal matter.

Non-living organic matter in water may have deleterious effects upon the animal system from its own action or that of its decomposition products, or it may serve as food for microörganisms of which the pathogenic bacteria are the most important. These are thrown off in the excreta from many infectious diseases like typhoid and can live a long time in water and communicate the disease by this means. Because of its frequent association with such organisms water which is contaminated with animal matter is regarded as more dangerous than that which contains a similar amount of vegetable products. Vegetable and animal substances remain if water is evaporated and when more highly heated they are discolored and blackened, often giving rise to offensive or characteristic odors. They are oxidized by potassium permanganate in the presence of sulphuric acid while they are in solution, the permanganate being at the same time decolorized. If the water has been proved free from nitrites or ferrous compounds, the action of which is the same, this may be considered a test for the presence of organic substances.

Qualitative Tests.

Calcium and Magnesium.

429. Make 50 cc.[1] of water alkaline with ammonium hydrate. If there is a precipitate of iron or aluminum remove it by filtration; otherwise to the liquid add ammonium chlorid and ammonium oxalate. A fine white precipitate of calcium oxalate forms slowly if but little calcium is present. If the precipitate is more than is obtained in the test for sulphates it indicates that a part of the calcium is probably in the form of a carbonate. Let it settle in a

[1] The volumes of water directed to be used in tests may often be increased if the supply is large, thereby making the results more accurate. Except in quantitative tests they need not be accurately measured.

warm place, then decant or filter and test the filtrate for magnesium by the addition of sodium phosphate. A white crystalline precipitate of ammonium magnesium phosphate appears.

Iron.

Examination should be made for both the ferrous and the ferric forms.

430. To detect ferrous compounds add a few drops of a dilute solution of potassium ferricyanid and acidify with hydrochloric acid. A blue color is produced. The reagent does not react in this manner with ferric salts. The ferric compounds may be shown to be present, after acidifying with hydrochloric acid, by the production of a red or pink color by the use of potassium sulphocyanate which remains colorless with ferrous iron.

Poisonous Metals.

431. Lead is the one which is most frequently suspected from its use in pipes, and occasionally it is desirable to test for copper or zinc. With any considerable quantity of the first two, hydrogen sulphid gives a brown or black color. It will usually be advisable before adding the sulphid to evaporate to about one-tenth of its bulk as much as a liter of water after acidifying with hydrochloric acid, and the use of hydrogen sulphid gas is here preferable to its solution, to avoid dilution. If a black precipitate is obtained, it can be removed by filtration and identified by the method of Table IV. The zinc can be separated from the filtrate or, in absence of a precipitate with hydrogen sulphid, from the concentrated water by first making the liquid slightly alkaline with ammonium hydrate, then passing in hydrogen sulphid and warming. It forms white, voluminous zinc sulphid which may be identified by its reactions.

Ammonia.

432. Ammonia does not occur in natural waters in sufficient abundance to render possible its detection by its odor or by litmus paper. Very minute quantities, however, yield a yellow to brown color with Nessler's reagent. If the amount is considerable there is a brown precipitate, but in ordinary waters the liquid remains clear. The result is somewhat complicated by the presence of calcium and magnesium compounds as they are in part precipitated at the same time. The difficulty can be completely overcome by distilling a part of the water from a retort and condensing the steam. The pure ammonia is found in the distillate.

In the detection of slight shades of color, or in estimating their intensity, the desired result can be best attained by using a test-tube placed above a piece of white paper and looking down into the tube.

Chlorin (Chlorids).

433. Acidify 30 cc. of the water with nitric acid and add a few drops of a solution of silver nitrate. An opalescent or milky liquid is produced or, with large amounts of chlorin, a white precipitate of silver chlorid. This dissolves in ammonium hydrate and is reprecipitated from this solution if it is acidified by nitric acid. Ordinarily there is too little chlorin to immediately give a precipitate. If this occurs the amount is excessive.

Sulphates.

434. Acidify 30 cc. of water with hydrochloric acid and add barium chlorid. Fine white barium sulphate precipitates, settling slowly, and in very dilute solutions appearing only after standing some minutes. It is insoluble in acids.

Nitrous Acid or Nitrites.

435. In the absence of ferric compounds the following may be used but not if ferric salts are present. To 30 cc. of water add two or three drops each of solutions of starch and potassium iodid, then acidify with about ten drops of dilute sulphuric acid. Nitrous acid sets iodin free which with the starch forms a blue color.

Ferric salts do not interfere with the next two tests.

436. Add to 30 cc. of water 1–2 cc. of dilute sulphuric acid and 1 cc. of a solution of meta-phenylen-diamin sulphate, which latter must be colorless. The appearance of a yellow to brown color indicates the presence of nitrous acid.

437. 20 cc. of water with 2 cc. of alpha-amido-naphthalene (napthylamin) acetate and 2 cc. of sulphanilic acid dissolved in acetic acid gives a pink or red color, varying with the amount of nitrites present. It should be allowed to stand five minutes to develop this fully.

The last two tests are much more sensitive than the first, so much so that extreme care must be used that neither they nor the vessels which contain the water are contaminated by nitrous acid from the atmosphere. The third test will detect one part of nitrous acid in one hundred million parts of water. On the other hand if the starch test is distinct, in the absence of iron compounds, it is probable that a considerable amount of nitrous acid is present.

Nitric Acids or Nitrates.

If nitrous acid has been found by the preceding tests it must be removed before examining for nitric acid as it will give most of the reactions for the latter. Evaporation of the water to dryness after the addition of a small pinch of ammonium chlorid decomposes the nitrites but not the nitrates.

$$NaNO_2 + NH_4Cl = NaCl + 2H_2O + N_2.$$

The evaporation can be performed in a porcelain dish. To avoid the possibility of overheating at the last, when it has been reduced to a small volume it should be placed upon a beaker of boiling water and heated thus until it is dry. The residue can then be dissolved in pure water and the solution tested for nitrates. They will readily go into solution although some of the other solids may remain.

438. To 30 cc. of water add enough indigo solution to impart a pale blue color, acidify with sulphuric acid and heat to boiling. If nitrates are present the blue color is discharged or diminished.

439. In a porcelain dish containing 2–3 cc. of water place a small crystal of brucin, then add an equal volume of concentrated sulphuric acid, stirring gently with a glass rod. A red color indicates nitric acid.

440. In the same manner as in the last repeat the test using a small crystal of di-phenyl-amin instead of brucin. Nitric acid or its salts give a deep blue color. With one part in 100,000 it is seen immediately; when twice as dilute it does not appear at once.

The test with indigo is not nearly so sensitive as the two last but only responds when a considerable amount of nitrates are present. The concentrated sulphuric acid of the trade, even the so-called chemically pure, frequently contains nitric acid and should be proved to be pure previous to using in all the above tests. If not so the nitric acid may be expelled by boiling for half an hour until it remains colorless when tested with diphenyl-amin.

Hydrogen Sulphid.

441. Acidify slightly 50 cc. to 100 cc. of water with sulphuric acid and boil for some time in a small flask in the neck of which is suspended a strip of white filter paper previously moistened with a solution of lead acetate. A

yellow or brown discoloration of the paper indicates hydrogen sulphid.

Organic Matter, Vegetable and Animal.

Many of the organic compounds which are found in water are readily oxidized, even when dissolved, by such reagents as potassium permanganate. This loses its red color at the same time. A few inorganic substances have also the ability to decolorize permanganate, those which may be present in natural waters being sulphids, nitrites and ferrous compounds. If these are absent or in very small amounts, water which decolorizes more than a few drops of a permanganate solution may be considered to contain some form of organic matter.

442. Acidify 50 cc. to 100 cc. of the water in a beaker or porcelain dish with 5–10 cc. of dilute sulphuric acid, heat to boiling, and while hot drop in the permanganate solution until a permanent pink tint remains. Compare the result with that obtained in the same manner from from a similar quantity of distilled water.

In addition to the decomposition products already discussed there are produced in water by bacterial processes small amounts of a number of compounds of which the most common are indol, phenol and their derivatives. Griess has proposed a method of detecting these by the intensely yellow color which they yield with diazo compounds. They are very abundant in water which is polluted with decaying animal matter or animal excreta. They may, however, be formed by vegetable matter, their source being the proteid compounds which are found in both, but less abundantly in the latter.

443. Make alkaline with sodium hydrate 25 cc. of water and add a few drops of a freshly prepared dilute solution of para-di-azo-benzene sulphonic acid. The liquid be-

comes yellow if the water contained decomposing animal matter or sometimes with large amounts of vegetable matter. The reagent cannot be preserved in solution but must be dissolved only when it is to be used. With the alkali and distilled water there should be thus produced no color although this may occur if the sodium hydrate is impure. A test should therefore first be made with distilled water to ascertain the purity of the reagents.

Quantitative Determinations.

Total Solids.

The amount of solid matter dissolved in a water is sometimes of importance. This can be ascertained by evaporating to dryness on a steam-bath a definite volume in a weighed dish and, after cooling, weighing the dish with the residue. With a sensitive balance 100 cc. of water is enough in most cases but, if the balance will not weigh to a milligramme, more may be taken. A large amount of dissolved solids is indicative of contamination although not conclusive. Mineral waters are, of course, an exception. The nature of the residue is indicated if it is more strongly heated after weighing. This is best done in a platinum dish but may be accomplished in one of thin porcelain. Much organic matter will turn brown or black and may give a more or less characteristic odor. Mineral substances are not discolored with the exception of iron which may be brown. After the organic matter has burned off they can be dissolved in hydrochloric acid (except silica) and identified by their qualitative reactions.

Ammonia.

The exact determination of ammonia is effected by distilling it from a large volume of water in a retort. The con-

densed steam contains the ammonia. By comparing the color produced in it by Nessler's reagent with that obtained by the same reagent in pure water to which has been added a known weight of ammonia, its amount can be estimated. The process requires special apparatus as well as a considerable skill in manipulation.

Chlorin.

444. To determine the quantity of chlorin use a standard solution of silver nitrate with normal potassium chromate for the indicator as described on page 185. For convenience in calculating results instead of the usual strength the silver solution may be made to contain 4.79 grammes of silver nitrate per liter. One cubic centimeter of this will precipitate one milligramme of chlorin. Of ordinary well water 100 cc. may be used. In this case each cubic centimeter of the silver solution necessary indicates one part of chlorin in 100,000 of water. With water of great purity it may be necessary to concentrate a larger volume, such as a liter, before titrating.

Nitrites.

When solutions of nitrites are treated with sulphanilic acid and naphthylamin an intense rose-red color appears varying with the amount of nitrite present. By comparing it with a solution of nitrite of known strength it is not difficult to judge the amount of the latter.

The reagents used are:

Sulphanilic acid, 0.5 grm. dissolved in 150 cc. of 3-per-cent. acetic acid, and

Naphthylamin — 0.1 grm. of the solid boiled with 20 cc. of water and filtered hot through a small filter, previously well washed to remove nitrites, then the filtrate diluted with 180 cc. of 3 per cent. acetic acid.

Standard sodium nitrite, 0.049 grm. of pure sodium

nitrite dissolved in one liter of water.[1] One cubic centimeter of this contains 0.01 milligramme of nitrogen. If it cannot be obtained pure in the dry state it can be made by dissolving the corresponding (molecular) weight of silver nitrite in a small volume of water and adding a solution of pure sodium chlorid as long as a precipitate forms, then diluting to the desired amount. It must be kept in the dark. The reagent bottles and all vessels used in the test must be rinsed with nitrite-free water.

445. To exactly 10 cc. of the water in a test-tube add 1 cc. each of the solutions of sulphanilic acid and naphthylamin and let it stand five minutes. If it is pink, in another test-tube dilute 1 cc. of the standard nitrite solution to 10 cc. and test in the same manner. Dilute the darker of the two until equal volumes are the same shade and from the amount of dilution calculate the amount of nitrite in the water as compared with that of the standard, and from this, the absolute weight of N in nitrites in 10 cc. and in a liter. Reduce this to parts per million remembering that one milligramme per liter equals one part per million.

Nitrates.

These can be quantitatively determined by their action upon phenolsulphonic acid, which is changed into picric acid, the ammonium salt of which has an intensely yellow color. Besides a standard solution of a nitrate for comparison but one other is needed.

Phenolsulphonic acid is prepared by mixing 3 cc. of water with 6 grammes of pure phenol ("carbolic acid"), then adding 37 grammes of pure sulphuric acid. The solution keeps well. If it in time crystallizes it can be redissolved by warming gently.

[1] Since this would be difficult to weigh accurately it is better to dissolve 0.49 grm. in 100 cc. and dilute 10 cc. of this to 1000 cc. before using.

Standard potassium nitrate can be made by dissolving of this salt 0.722 grm. in a liter of water. 1 cc. of this contains 0.0001 grm. of nitrogen or one part in ten million.

446. Evaporate to dryness on a steam-bath a definite volume of the water — 25 to 100 cc. according to whether the qualitative test showed much or little nitrate present. To the residue add 1 cc. of phenolsulphonic acid and, after thoroughly mixing, 1 cc. of water and three drops of concentrated sulphuric acid. The whole is warmed two or three minutes on a steam-bath. After cooling add 20 cc. of water and make alkaline with ammonia. Treat 1 cc. of the standard solution in the same manner and compare the colors in large test-tubes, diluting until they are the same and computing the amount of nitrogen in the nitrates in parts per million, as with nitrites above. In the whole process the water and sulphuric acid used must be known to be free from nitric acid and its salts, as discussed under the qualitative tests.

Organic Matter.

The amount of this can be only indirectly determined because of the variable nature of that which may be present. The degree of discoloration or charring, also the odor, of the heated residue after evaporation, may give some indication of it. Other methods are to determine the exact quantity of organic carbon or nitrogen in the water and to use them as measures of the vegetable and animal matter. Instead of these it is more convenient, and perhaps as accurate, to find the amount of oxidizable matter and, deducting the nitrites and ferrous compounds, also the sulphids, if they are present, to regard the remainder as organic. A suitable oxidizing agent for this purpose is a solution of potassium permanganate which readily gives up its oxygen in an acid liquid, becoming at the same time colorless.

447. A rough estimate can be made of the amount of oxidizable matter by acidifying 50 or 100 cc. of the water with 10 cc. of dilute sulphuric acid, heating to boiling, then counting the number of drops of centinormal potassium permanganate necessary to color the boiling liquid permanently pink. The reagent can be dropped slowly if the stopper is held loosely without removing it from the bottle. For comparison the same test may be tried on an equal volume of distilled or other pure water.

448. For more accurate results a centinormal solution (0.395 grm. per liter) of potassium permanganate may be used with a corresponding one of oxalic acid, so that one cubic centimeter of the latter shall decolorize exactly one of the former. To 100 cc. of the water in a 250-cc. flask add 20 cc. of dilute sulphuric acid, then from a burette, 10 cc. of the permanganate or enough to give a permanent red color to the water after it has been boiled 10 minutes. This should be accurately measured. When it has been boiled 10 minutes add from another burette a volume of centinormal oxalic acid equal to that of the permanganate used, when the red will disappear. Now drop in more permanganate from the first burette, while stirring, until a permanent pink color is produced. The volume of permanganate last added corresponds to that destroyed by the oxidizable substance in the water. One cubic centimeter contains 0.1 milligramme of available oxygen, and the final results should be expressed in terms of this.

Owing to the fact that there is a great variation in the ease of oxidation of different kinds of organic matter as well as in their content of carbon and nitrogen, the results obtained should be regarded as only approximate although they are often of great value in arriving at a conclusion as to the purity of the water. For the properties of the standard solutions of permanganate and oxalic acid refer-

ence should be made to their previous description under Oxidimetry.

Interpretation of Results.

Calcium, magnesium and iron are comparatively unimportant in water from the sanitary standpoint although when excessive they greatly lessen its value for domestic purposes, the two first because they render it hard, and the last because it deposits as a brown ferric hydrate. They all more or less modify the taste. The sulphuric acid, as found in sulphates, if united with the calcium makes the water permanently "hard," that is, this compound is not precipitated by boiling, as is the carbonate. Small amounts of sulphates are otherwise not of much consequence. Considerable quantities of the sulphates of magnesium, and sodium cause the water to act as a laxative.

It is only exceptionally that ammonia is absent from natural waters. It signifies that, probably by bacterial action, nitrogenous organic compounds, vegetable or animal, have been decomposed, the latter yielding more than the former. When nitrites are found, bacterial action upon these compounds is in progress, although the bacteria are not necessarily of the pathogenic varieties. Nitrates are the final products of such action, unless they are again reduced to nitrites. When found alone they indicate some past pollution by nitrogenous substance — animal or vegetable. Chlorin occurs rather abundantly in the soil near the sea and in parts of the country where there are salt deposits or brines. It then loses much of its value as an indication of contamination. Since, however, water drawn from the same stratum in the same section has practically the same composition unless it is contaminated, a comparison of the amount of chlorin in the water of one well with that of surrounding ones will often show whether it is excessive or not. Neglecting that of the soil, it is an evidence

that pollution has occurred from animal matter, probably sewage. This is of course pollution of the most dangerous kind, still if chlorin alone is found it may be that the accompanying organic matter and bacteria have been filtered out by the soil, or oxidized by the air, and that the water will not communicate disease; in other words it is an evidence of past contamination. Chlorin in itself has no poisonous action but its presence is suspicious. Hydrogen sulphid can be produced by the breaking down of organic sulphur compounds like the proteids, or by the action of decomposing organic matter on the sulphates, whereby the latter are reduced. Hence it usually shows that a considerable organic matter is or has been contained in the water.

Decolorization of the potassium permanganate solution, in the absence of reducing agents like nitrites, sulphids, or ferrous compounds, indicates organic matter, either animal or vegetable. Para-diazo-benzene-sulphonic acid in alkaline solution (Griess' test) shows the presence of compounds such as result from the putrefaction of albuminous matters. These are abundant in the excreta and decaying animal tissues but may be produced also from similar changes in the vegetable albuminous substances. In the last case they are only found in comparatively small amounts.

We might then expect to find with water containing fresh vegetable matter a little ammonia and some reduction of the permanganate solution but no reaction to Griess' test and an absence of more than traces of chlorin, nitrites and nitrates. As it decays the ammonia increases and the reduction of the permanganate diminishes until there may be none. There will finally be a conversion of most of the nitrogen into nitrates with possibly a slight amount of nitrites. It is seldom that all the ammonia disappears.

Animal matter (excreta or tissues), while decomposition is in progress, reduces the permanganate solution and gives Griess' reaction if in sufficient quantity. Chlorin and ammonia are then abundant, nitrites are often present and sometimes nitrates. As the decomposition progresses the permanganate and Griess' tests give less marked results and the nitrates increase. The quantity of chlorin is not affected.

The source of the water will also somewhat modify the conclusions to be drawn from the analysis. Thus deep well water often contains much chlorin from the rock formations with which it comes into contact. More ammonia may be allowable here than in surface or shallow well waters since it has no means of escape and the conditions are unfavorable for bacterial life. It is produced here by the reduction of nitrates through the action of organic matter. Nitrates are occasionally found plentifully in deep waters, being derived from the remains of fossil organisms. This is especially seen in Cretaceous rocks. On the other hand organic matter is usually absent or in traces. Rain water absorbs much ammonia and sometimes nitrites from the air and these then lose their customary significance, being no longer indicative of organic decomposition. In the water from deep wells (artesian) also nitrites may be formed through the reduction of nitrates by organic matter without the aid of bacteria and then are unimportant.

Standards of Comparison.

From what has been said regarding the modifications which surrounding conditions produce in the composition of water it is obvious that we can not establish any absolute standards which shall apply to that from all sources. Nevertheless it is a matter of great convenience to be able to compare the composition of one under observation with

that of others the nature of which has been determined. Such figures must be used carefully with a full understanding of the influences that may change them. Knowing, then, that the standards represent only the amounts of impurities which have been found to be present under different conditions we can employ them as aids to the formation of an opinion as to the significance of our analyses.

The following may represent the composition of some varieties of drinking water in which the figures represent parts per million.

	Good, less than	Suspicious.	Bad, over	Milligrams per Liter.	= Parts per Million.
Total solids.	500	500–700	800		
Chlorin.	5	10–20	25	$NaCl$, 23	Chlorin, 15.
Nitrogen in nitrites.	0	0.02	0.04	$NaNO_2$, 0.1	Nitrogen in nitrites, 0.02.
Nitrogen in nitrates.	0.5	1.0–2.0	5	KNO_3, 1.4	Nitrogen in nitrates, 2.0.
Ammonia.	0.05	0.06–0.1	0 15	NH_4Cl 0.3	Ammonia, 0.1.
Cubic centimeters of $\frac{N}{100}$ $KMnO_4$ reduc'd by 100 cc. of water.	1.5	3–4	8		

Solutions made up of the above strengths by the aid of the last two columns, may serve for comparison so that the more accurate quantitative methods of determination can, at times, be dispensed with.

Practical Exercises in Water Analysis.

Make chemical examinations of samples of water furnished by the instructors. Hand in written reports giving the presence or absence, also comparative amounts (small, moderate or large) of the following:

1. Calcium.
2. Magnesium.
3. Iron, ferrous and ferric.
4. Lead, copper or zinc.
5. Ammonia.
6. Chlorin.
7. Sulphates.

8. Nitrous acid (nitrites).
9. Nitric acid (nitrates).
10. Organic matter by general tests.

Tell what you can about the past history of the water. If it contains organic matter is this vegetable, decaying animal or sewage? Is the water suitable for drinking, to be condemned, or merely suspicious? Is it suitable for other purposes than for drinking? Give reasons for your conclusions.

CHAPTER II. THE DETECTION OF POISONS.

THE testing of substances for the detection and identification of poisons, although it may be properly considered in a separate chapter from general analytical chemistry, is not a different branch of chemistry, but makes use of many of the principles and operations already considered.

Its importance lies in the value of the evidence of the chemist as a proof of attempted or accomplished poisoning, and in the fact that this is often the strongest, and sometimes the only, evidence obtainable. It differs from the more common methods of analysis in the nature of the materials which are investigated, these being often complex mixtures of organic and inorganic compounds, such as medicines, foods, vomited matter, saliva, urine, blood or animal tissues. In these the poison sought is ordinarily comparatively very small in amount. Not only must the presence of a poisonous element be shown, but that it is in a combination dangerous to the animal body. For example, most sulphates are harmless, whereas the acid from which they are derived is a violent poison. It is, moreover, frequently desirable to determine not only the kind but the amount of such compounds in the substance analyzed.

Some of the difficulties encountered in testing for poisons are that their minute amount renders many of the common reagents ineffective, that the presence of other compounds, especially organic matter, interferes with their giving the expected reaction, that their separation from such compounds and purification requires much time and care, that during the necessary operations they may vola-

tilize, as does prussic acid, or undergo decomposition, like the alkaloids or become converted into a harmless form like phosphorus. Still, for many of them, the means of identification, if properly carried out, are as effective as any analytical processes.

Since but a limited quantity of the substance is at the disposal of the analyst the tests should be applied at first to only a portion in order to have a reserve in case of accidents, or for further investigation, and it is better to note the weight of the whole and of the part used in order to be able to calculate the total amount present from the fraction that may be found in that part. To avoid a waste of material the most characteristic and reliable tests should be tried first. If possible the isolated poison or compounds of it should be preserved in such a way as to be submitted in a possible future trial. The question of the purity of the reagents is of the greatest importance. The different grades of "purified," "pure," "chemically pure" and "absolutely chemically pure" do not necessarily guarantee the same quality when they are made by different manufacturers. It will be necessary to prove their purity or to make with them a blank test — that is to go through the operation with the chemicals alone without the addition of the suspected substance, when, if they are of satisfactory quality, the result should be a negative one. The reagents in common use may suffice for the usual methods of testing and fail to give satisfaction when a hundred or a thousand times the ordinary quantity of them must be employed. All other materials, such as filter paper, rubber tubing or apparatus, must also be known to be free from objectionable substances.

There follows a list of the reagents of most frequent use in toxicological investigations, with a discussion of their impurities.

Water.

This should of course be distilled but as occasionally such water contains traces of the heavy metals it should be tested by evaporating a liter to dryness. There must be left only a minute residue and this, after dissolving in 5–10 cc. of water must give no precipitate with hydrogen sulphid or ammonium sulphid. Distillation is best conducted in a tin-lined vessel and the steam condensed in a tin pipe.

Hydrochloric Acid.

This should, after dilution, give no precipitate upon saturation with hydrogen sulphid or, after neutralization, with ammonium sulphid. Its most dangerous contamination is arsenic, which is not infrequent. Very large amounts of the acid are used in the destruction of organic matter and hence a comparatively large quantity of arsenic may be introduced even if but a small fraction of a per cent. is contained in the acid. It cannot be regarded as of satisfactory purity unless after about a liter is concentrated to a small volume (10 to 20 cc.) by evaporation in a well-ventilated hood and 5 cc. of the remaining liquid is tested with Gutzeit's test (118) no yellow color with brownish-black margin appears on the paper within half an hour. It may be further tested by Bettendorf's (120), Reinsch's (117), or Marsh's (121) tests.

Sulphuric Acid.

This is not used in such large amounts as the hydrochloric and there is consequently less danger of introducing impurities with it. Its principal use is in Marsh's test for arsenic. It occasionally contains lead as well as arsenic. The lead will be shown by the yellow or brown color produced by saturating the dilute solution with hydrogen sulphid gas. For arsenic it can be tested, after diluting with

four times its volume of water, by Gutzeit's (118), Reinsch's (117), or Marsh's (121) tests. With the latter 200 cc. of the acid, generating about a liter of hydrogen in fifteen minutes should show no mirror in the tube after half an hour's heating. When used in the alkaloidal tests it must be absolutely free from nitric or nitrous acid. Hence it should give no color with brucin (439) or di-phenyl-amin (440). These compounds if present may be removed by boiling as in 440.

Hydrogen Sulphid.

The materials commonly used in the preparation of hydrogen sulphid frequently contain arsenic. Either those which are free from arsenic should be employed or the gas must be purified. Passing it through a long tube over crystals of iodin forms arsenic iodid which remains in the tube.

Ammonium Sulphid.

This must be prepared from arsenic-free hydrogen sulphid, made in the above manner.

Ammonium Hydrate and Sodium Hydrate.

Arsenic and the heavy metals should be absent. When acidified with pure sulphuric acid no results should be obtained from Marsh's test, from the addition of hydrogen sulphid, nor after making alkaline by ammonium sulphid.

Potassium Chlorate.

This should be free from arsenic and the heavy metals. Dissolve 50 grammes in water and add pure hydrochloric acid as long as chlorin is evolved. Test half the solution by Marsh's test (121) and the rest by hydrogen sulphid (Table IV), and ammonium sulphid (Table II).

Ethyl Alcohol.

Metals and other basic substances must be absent. By

distilling over tartaric acid they can be separated if small amounts are present.

Amyl Alcohol.

It should leave no residue when evaporated, should boil at 131°–132°; and when shaken with dilute sulphuric acid should give to the latter nothing which gives the general alkaloidal reactions (pages 145–6).

Benzene.

This should have the boiling point of 79° and otherwise answer the requirements for amyl alcohol.

Chloroform.

Can be tested as the last. It should boil at 61°.

Petroleum Ether.

The boiling point should not be above 60°. No residue should remain when it is allowed to evaporate on a watch glass.

The filter paper employed should be white and the ash remaining after it is burned should be little and free from barium and the heavy metals. When the solutions must come in contact with the rubber tubing this must contain none of the poisonous metals. In the white tubing lead and zinc are often found and in the red, antimony. Black rubber is the preferable kind. Porcelain vessels are less liable to break than glass ones, also to attack by reagents, but they should not be used after the enamel is in any degree injured, and the enamel must contain no lead.

Outline of the Plan of Analysis for Poisons.

I. Preliminary examination.

II. Distill in the presence of an acid with the aid of steam — the volatile poisons, hydrocyanic acid, phenol (carbolic acid), phosphorus, chloroform, chloral hydrate.

III. Dry. Extract the dried residue with alcohol.
1. The alkaloids.
2. Oxalic and meconic acids and some mercury salts.

IV. Destroy the organic matter and test the solution for metals of which the compounds are poisonous.

I. Preliminary Examination.

Before proceeding to the systematic analysis a preliminary examination will be advantageous. This may be both physical and chemical. In the former, if the material is a complex mixture, like the contents of a stomach or vomited matter, its appearance should be noted, as to whether there is evidence of the presence of unusual substances. Sometimes the unaltered poison (vegetable or animal) may be thus detected. A low-power magnifying glass is of service. Phosphorus will be visible if the room is darkened, especially after the substance is dried and stirred in the air. Any odors should be noticed, as they may be characteristic of some compound sought. Not more than one-tenth of the available material should be destroyed in preliminary tests.

Reaction. — A strong acid or alkaline reaction to litmus paper may be due to mineral or oxalic acids or to a caustic alkali.

The above acids will be found in the aqueous extract and change a Congo-red solution to a deep blue. Oxalic acid changes the color of a methyl-violet solution to a blue. Hydrochloric acid of the strength found in normal gastric juice will do the same, also very dilute solutions of nitric or sulphuric acids. In any considerable amount the three last give with methyl-violet a green to yellow color. If a few cubic centimeters of the solution be slowly evaporated from a small test-tube with a few crystals of cane sugar

there will be with sulphuric acid a blackening or charring as the water is driven off; with nitric, an evolution of yellowish-brown oxids of nitrogen; with hydrochloric, a yellow, then brown color in the liquid, with the odor of the acid gas; with oxalic acid, no odor or colored gas, nor discoloration until the water has been expelled, when the sugar will be converted to caramel if the heating is continued.

Of the caustic alkalies ammonium hydrate will have already been recognized by its odor although it must be remembered that ammonia may be formed by the bacterial decomposition of nitrogenous matter. The sodium hydrate and potassium hydrate can be dissolved from dried residues by hot alcohol. They remain after this has been distilled. Solutions of these turn litmus paper blue and give a red color to a phenolphthalein solution. The alkaline carbonates do the same but not after an excess of barium chlorid has been added to the solution. The alkaline hydrates will act upon litmus and phenolphthalein after the addition of barium chlorid as well as before.

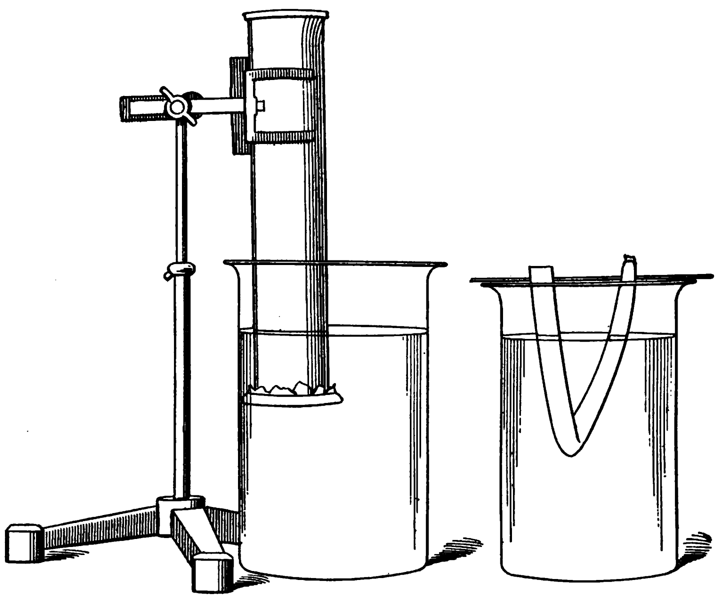
Test for phosphorus and hydrocyanic acid in a partly filled flask with lead acetate paper (453) and silver nitrate paper (453) also guaiacum paper (449) and watch glass tests (450 and 452*a*).

Dialysis of a portion of the mass may render possible the classification of the poison. Place the substance in a dialyzer,[1] after thinning with water and slightly acidifying with nitric acid, and let this stand 24 hours in four or five times its volume of water. The liquid outside is then concentrated, if desirable, and examined for some of the

[1] The dialyzer may consist of a wide, glass tube which has one end closed with a membrane of animal or vegetable parchment. The substance to be dialyzed is placed in this and the whole is suspended in a vessel of water so that the level inside and out is the same. Or, instead of this, a parchment tube containing the substance may be suspended from the ends in the water.

groups of poisons, one portion being tested by hydrogen sulphid for the heavy metals, another for the alkaloids, by

FIG. 18.



Two forms of dialyzers; the first an open glass tube with parchment end, the second a tube of parchment paper.

means of the general reagents (page 245), another for the acids or alkalies, etc.

If in the preliminary tests some indication has been obtained of the class of compounds the search should be made first for these. If no indication had been obtained of the class to which the poison may belong a systematic examination must be undertaken for all that can be present. For this the remaining material may be divided into four parts and one examined for each class of compounds unless the poison is found sooner, one being

reserved for emergencies or confirmatory tests. The plan of analysis given will serve as a general guide for work, although the chemist will often modify it in accordance with his observations during the progress of the analysis. It is far from including all poisons but it may be used in the search for the more common. For a complete course of analysis reference should be made to some larger work, such as that of Dragendorff.

II. Poisons Distilled from an Acid Liquid.

Dilute the finely divided mixture into a thin fluid with water, then add enough dilute sulphuric acid to merely give an acid reaction. Distill from a retort on a water-bath, towards the last of the operation passing in steam from a flask through a tube which extends nearly to the bottom of the liquid. The distillate must be well cooled by a long Liebig's condenser.

Hydrocyanic Acid.

(Ferrocyanids and ferricyanids must be absent or the tests are not conclusive.)

The volatile acid has the characteristic odor of bitter almonds, and appears in the first stages of the distillation.

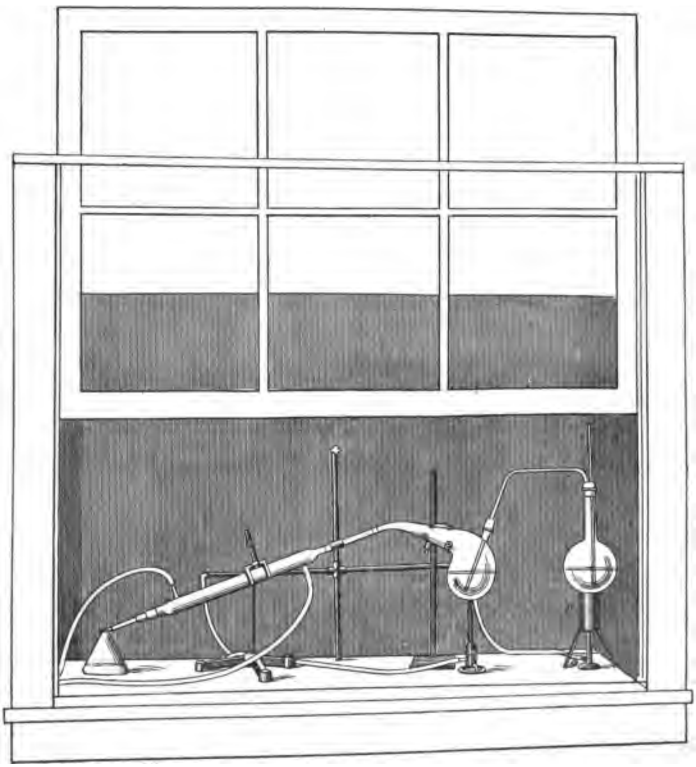
449. The gas or a drop of the distillate turns blue a white paper previously moistened with very dilute copper sulphate solution and an alcoholic solution of guaiacum resin. There are a few other substances which give a similar result but they are not commonly present.

450. With silver nitrate a white precipitate is produced, which dissolves in ammonium hydrate or sodium hydrate and is reprecipitated therefrom by nitric acid in which it is insoluble. It is not discolored by light like silver chlorid (239). To remove any hydrochloric acid which may have been distilled over from the retort, before testing with the

silver nitrate, the distillate can be shaken with a little powdered borax and redistilled.

451. The distillate forms Prussian blue with iron salts when treated according to 247.

FIG. 19.



Apparatus for distillation with the aid of steam. This is passed into the liquid in the retort by a tube which enters through the tubulure. The flask at the left in which the steam is generated is provided with a straight safety-tube, open at both ends. This allows air to enter if the heating is interrupted and thus prevents the liquid in the retort from being drawn back. The neck of the retort is connected with a Liebig's condenser and the whole apparatus stands in a hood which is provided with a flue and a sliding door so that obnoxious gases are removed from the room.

452. To a few drops of the distillate add 2 or 3 drops of a solution of potassium nitrite and as much ferric chlorid. Drop in dilute sulphuric acid until the brown color becomes a yellow and warm gently. Cool, precipitate the iron with a few drops of ammonium hydrate, filter, and to the filtrate add one drop of very dilute ammonium sulphid. A violet color appears, changing to blue, green and yellow. The hydrocyanic acid has been converted into a nitroprussid which gives the above results with sulphids. Less than one part in a million can be thus detected.

452*a*. Place between two watch-glasses adding H_2SO_4 if testing for a cyanid. Moisten the under surface of the upper glass with yellow ammonium sulphid solution and allow to stand 10 minutes. Ammonium sulphocyanate is formed on the upper glass. Remove this and dry on a water-bath. Very dilute ferric chlorid gives a red color with the residue after acidifying with HCl (64).

Phenol. (Carbolic Acid.)

As this is less volatile than the hydrocyanic acid the latter portion of the distillate can be used for testing. With this try the phenol reactions (page 134).

Chloroform.

If much is present it will appear as colorless drops with the characteristic odor, unless the latter is hidden by other compounds. Try the test with anilin and potassium hydrate (277) and if necessary confirm by 278.

Chloral Hydrate.

The distillate gives no odor of chloroform until it has been warmed with an alkali. Test with resorcin (319), ammonium sulphid (320) or with sodium hydrate (316).

Phosphorus.

Carry on the distillation in a perfectly dark room. Notice the luminous ring in the condenser (454). For a

confirmatory test use the color of the flame with hydrogen generator (455), also effect on silver nitrate paper (453) as directed below.

The yellow variety of phosphorus is the one which acts poisonously. Its odor and luminous appearance in the dark are characteristic.

453. When an acidified liquid or mass containing phosphorus is placed in a flask of such a size that it shall be at least three fourths filled with air and from the loosely inserted stopper strips of filter paper are hung which have been moistened, one with a solution of lead acetate made alkaline with sodium hydrate, and the other with silver nitrate, the latter is darkened slowly by the reduction of the silver salt by the vapors of phosphorus. The former is unaffected. Hydrogen sulphid blackens both papers and its presence destroys the value of the test. Failure of the paper to darken indicates the absence of phosphorus. The flask should be allowed to stand a considerable time in a dark place before the conclusion of the test.

454. If a mixture containing phosphorus is diluted to a liquid with water then, after acidifying, is placed in a retort and distilled in a dark room by passing steam through it, the vapors being cooled by a Liebig's condenser, at the point where the steam is condensed there appears a phosphorescent ring. This moves back and forth in the condenser and may be visible a long time. Very minute amounts of phosphorus may be thus detected, but the phosphorescence is prevented by mercuric chlorid, alcohol and some other volatile substances. It appears, however, when these latter have been removed.

455. When treated in a Marsh's apparatus as described in the test for arsenic (121) phosphorus forms hydrogen phosphid, PH_3, which, when passed into silver nitrate solution, forms dark, insoluble silver phosphid mixed with

metallic silver. This compound can be filtered out and tested, after acidifying, by distillation as above. If the gas is passed through a tube filled with pieces of pumice saturated with sodium hydrate, for the purpose of absorbing the hydrogen sulphid which may be present, the flame of the ignited gas is greenish. It should not be lighted until the air has been completely expelled and should be burned from a small metal tube like a mouth blow-pipe to avoid the color which the sodium of the glass would impart. The color can be made more perceptible by holding a cold porcelain dish in the flame.

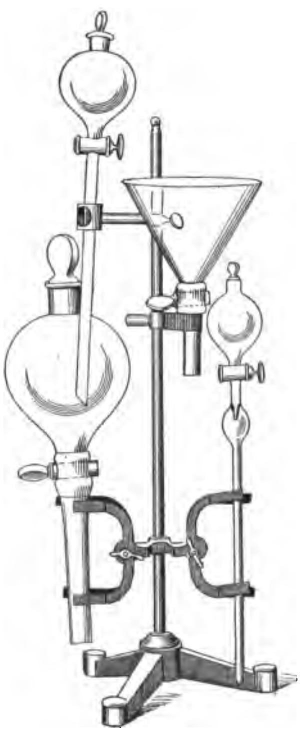
III, 1. Examination for Alkaloids.

To another portion of the finely divided mass add so much dilute sulphuric acid that the reaction is faintly acid (but not more than 5 cc. of 20 per cent. acid for each 100 cc. of the liquid). Mix thoroughly and let it stand several hours at 40° to 50°, then filter through a cloth. Repeat the extraction, uniting the filtrates. Evaporate on a steam-bath to a thin syrup but no farther; dilute with 3–4 times its volume of 90–95 per cent. alcohol, which dissolves the alkaloidal sulphates, and filter after it has stood 24 hours. Pour the filtrate into a flask and distill off the alcohol on a steam-bath. The sulphates of the alkaloids remain. Test a portion for these, reserving some for III, 2; III, 3; and III, 4.

The alkaloids and some other organic poisons can be, to some extent, classified and separated by the differences in solubility of their salts and of the free substance in certain organic solvents. When the aqueous liquid is mixed, without too violent shaking, with the solvent, and the mixture is allowed to stand, the solvent, which is selected so as to be lighter or heavier than the original fluid, removes from this liquid the alkaloid. By performing this operation in

a separatory funnel or a burette with a glass stop-cock one liquid can be separated from the other. To ascertain if anything has dissolved, or to test it, a drop of the solvent after separation can be allowed to evaporate on a watch crystal. The steps in this separation are:

FIG. 20.



Different forms of separatory funnels used for separating a liquid from another in which it is insoluble.

(*a*) If necessary add water until the acidified solution is not syrupy, then shake in a separatory funnel with petroleum ether, repeating until the soluble matter has been dissolved.

The petroleum ether contains some of the coloring matters, also the fats, and the phenol which was not removed by distillation.

(*b*) To the solution from which the petroleum ether has been separated add sufficient ammonium hydrate to make it strongly alkaline. The alkaloids are set free and, if in large amounts, may appear as a precipitate. Whether this is so or not, shake the liquid with more petroleum ether, separating as before, after standing long enough for the petroleum ether to have completely risen to the top of the aqueous solution. If a residue remains when the petroleum ether has spontaneously evaporated in a watch-glass, it may be cocain which is in white crystals. If such a residue remains treat the liquid with

the petroleum ether as long as a drop leaves any solid when evaporated. Test the residues by the cocain reactions (page 151).

(*c*) In the same manner shake the solution remaining from the petroleum ether extraction with benzene (benzol, C_6H_6), letting the benzene evaporate on a number of watch-glasses without heating. To learn if an alkaloid is present dissolve in water with a drop of acid and apply the general alkaloidal reagents (page 145).

There may be contained in the residues from the benzene atropin, brucin, narcotin, strychnin and veratrin. Observe the appearance and, if the general alkaloidal reagents (page 145) show the presence of alkaloids, test the separate portions with a drop of concentrated sulphuric acid and another of concentrated nitric acid.

	Usual Form.	H_2SO_4. Concentrated.	HNO_3, Concentrated.	Tests on Page.
Atropin,	crystalline,	colorless,	colorless,	150
Brucin,	amorphous,	colorless,	deep red,	149
Narcotin,	crystalline,	colorless,	yellow,	148
Strychnin,	crystalline,	colorless,	yellow,	148
Veratrin,	amorphous,	yellow, orange, then red (414)	yellow to colorless.	151

Confirm the indicated alkaloids by the individual reactions.

(*d*) The solution which has been treated with benzene is to be shaken with amyl alcohol and, after separating, the latter is to be evaporated on the steam-bath.

Morphin remains as a crystalline residue. Confirm it by its characteristic reactions (page 147).

III, 2. Examination for Oxalic Acid.

A part of the alcoholic solution from the dried substance is filtered and evaporated to dryness on the steam-bath and the residue dissolved in water. This solution, if oxalic acid

is present, gives calcium oxalate with calcium chlorid (190); it decolorizes potassium permanganate (191); oxalic acid precipitates from a solution of gold chlorid metallic gold in scales (144). Other tests have been referred to in the preliminary examination.

III, 3. Examination for Meconic Acid.

Test with silver nitrate (333) and ferric chlorid (332). The latter is the more characteristic.

III, 4. Examination for Metallic Compounds Soluble in Alcohol, Especially those of Mercury.

Although the general tests for the metallic compounds are made with another portion of the substance this solution may be tested with hydrogen sulphid and the test completed in the usual manner (Table III). Since only substances soluble in alcohol can be present here the discovery of a metal affords some indication of the original compound.

IV. Metallic Poisons.

They may include compounds of arsenic, antimony, lead, copper, mercury, silver, zinc and barium.

These may be sought in the residue from the alcoholic extraction of III (except lead and barium) or another portion of the mass under investigation. In order to obtain them in a sufficiently pure state to identify them any organic matter present should be first destroyed. This is accomplished through oxidation by means of chlorin. The finely divided mass is diluted to a thin mixture with pure, concentrated hydrochloric acid, and a little water. Place it in a flask which it must no more than half fill, and drop in from time to time a little powdered potassium chlorate as long as the fluid has a dark color, assisting the oxidation toward the last by warming on the steam-bath.

Avoid the use of unnecessary amounts of either acid or chlorate. Cellulose or masses of fat, which are difficult to decompose, may be filtered out and the filtrate employed for the examination.

The clear liquid is freed from chlorin by passing carbon dioxid through it and afterwards saturated with hydrogen sulphid. This may be done in a flask fitted with a two-holed rubber stopper and two tubes. The entrance tube is connected with the generator and extends to the bottom of the solution. Gas is passed in, for 24 hours (111), the liquid being warmed and shaken occasionally. The zinc and barium alone remain unprecipitated. Filter and wash.

Compare the color of the precipitate with that of the sulphids of metals possibly present. Separate or test it by the methods given in Table IV, confirming by the reaction of the individual metals, using for the latter purpose a fresh portion of the solution if desirable.

Test the filtrate for zinc after the method of Table II and the zinc reactions (page 46). If this is not present or has been removed, test for barium according to Table I and the barium reactions (page 37).

Special Problems in Toxicology.

Detection of Arsenic in Milk or Liquid Foods. — Use Reinsch's test (117).

Detection of Arsenic or Lead in Urine. — Acidify about a liter with hydrochloric acid, saturate with hydrogen sulphid gas and let it stand in a corked flask for 24 hours. If there is a precipitate filter and wash it. If it is yellowish test for arsenic by Gutzeit's test (118). If black dissolve in a few drops of nitric acid and test for lead (159, etc.).

Detection of Mercury in Urine. — Acidify about a liter of urine with 1 or 2 cc. of hydrochloric acid, warm to 50°–

60°, add half a gramme of zinc dust or freshly precipitated metallic copper (81). Stir vigorously half a minute and then filter. Metallic mercury is precipitated (96). Wash and confirm by heating in a tube (96).

Detection of Copper in Coloring Matters. — Digest the fabric some time with strong ammonium hydrate. A blue solution indicates copper (78). Acidify and confirm with potassium ferrocyanid (80).

Detection of Copper in Foods. — A large amount will be precipitated from the mass, after acidifying with hydrochloric acid, by means of iron, like a bright knife blade (81). When this is washed and digested with concentrated ammonium hydrate it makes a blue solution. If the amount of copper is small it may be necessary to first destroy the organic matter by potassium chlorate (page 226).

Detection of Lead in Water. — Concentrate a large volume of water (one or more liters) to 100 cc. in a dish with lead-free glazing, after adding one drop of nitric acid for each liter. If it is discolored from organic matter remove this by potassium chlorate and hydrochloric acid (page 226). Then saturate with hydrogen sulphid gas, heat to boiling, filter and, after dissolving in nitric acid, confirm by lead tests (159, etc.).

Detection of Dangerous Amounts of Lead in Glazing or Enamel. — In the vessel to be tested boil for half an hour 4 per cent. acetic acid, adding water as it evaporates. Test the liquid after this time with hydrogen sulphid as above.

CHAPTER III. ANALYSIS BY MEANS OF THE BLOW-PIPE.

MANY of the important physical and chemical properties of the metals and their alloys which have not been shown by the preceding work can be demonstrated by the use of the blow-pipe (page 25). These are often of the greatest importance in the technical use of the metals or the manufacture of their alloys, and they can best be learned by careful observation and long practice. They are such as are imparted to the metals, or are modified by heating. By the same means some of the non-metallic elements and compounds undergo characteristic changes also.

Many metals, as well as some non-metallic substances, give characteristic reactions during or after heating alone or with some chemical agent. To obtain these first excavate a shallow cavity near one end of a stick of charcoal; place in this some of the substance equal to half a pea in size, and apply the blow-pipe flame, using first the oxidizing flame then the reducing (pages 25–26), and heating the charcoal underneath the assay as much as possible. The flame should be directed toward the unoccupied end of the charcoal so as to allow for a possible deposition of a coating.

In some cases the results are better observed if instead of the charcoal the assay is heated on a thin slab of plaster of paris, made by pouring a thick mixture of this with water into a pasteboard box and letting it harden. For light colored coatings it can, previous to using, be blackened by smoking.

I. The Non-metallic Substances and Metals of the Alkalies and Alkaline Earths.

Water, if present in large amounts in the form of water of crystallization, as in alum, causes the substance to melt easily. When it has been evaporated by continued heating the anhydrous substance remains on the charcoal. If only a small quantity of moisture is present it will be necessary to heat the powdered solid in a matrass when the moisture appears on the cool walls of the tube. Most hydrates give up their water in this way. Many nitrates and chlorates deflagrate when heated on charcoal, that is, appear to burn rapidly, leaving little visible residue. This is especially true of salts of the alkalies. Nitrates, when mixed with acid potassium sulphate and heated in a matrass evolve a yellowish gas, best seen by looking down into the tube. This gas turns brown a slip of filter paper which has been dipped in a solution of ferrous sulphate.

Chlorates yield oxygen, sometimes mixed with chlorin, when heated in a matrass. If cupric oxid is dissolved in a bead of microcosmic salt by the aid of the oxidizing flame, when a chlorate is added the flame becomes azure blue. Other *chlorin compounds* give the above reaction with the microcosmic bead and cupric oxid as do bromin compounds also. Many of them decrepitate, that is, fly to pieces when heated, because of the moisture that is contained in the crystals, though this is not characteristic of chlorids.

Free sulphur and sulphids oxidize on charcoal in the oxidizing flame with the evolution of sulphurous oxid, recognizable by its odor.

Sulphates and other sulphur compounds, if they are fused on charcoal with dry sodium carbonate, and if then the fused mass is placed on a silver coin and moistened,

will turn the coin brown to black from the presence of sodium sulphid.

Silicates when heated on charcoal give no characteristic results. If fused in the bead of microcosmic salt their bases dissolve and the acid floats in a skeleton-like mass in the hot bead.

Organic compounds usually blacken when heated although they do not always do so. If they contain no metals they are completely combustible or volatile.

Carbon can be burned completely. Graphite is combustible with difficulty before the blowpipe. It deflagrates when heated with potassium chlorate on platinum foil.

Sodium and potassium compounds melt and sink into the charcoal. Sodium gives a yellow flame; potassium, a violet one (page 32).

Ammonium compounds volatilize completely, leaving a distinct white coating on the charcoal.

The compounds of the *alkaline earths*, barium, strontium, calcium and magnesium, remain white on ignition and often become highly luminous. They are sometimes infusible and sometimes melt and sink into the charcoal. Compounds of these metals that reduce to the oxids will, after heating, turn moist litmus paper blue when placed upon it.

Barium when held in the blue flame colors it yellowish-green. This may be made more perceptible by moistening the substance with a drop of hydrochloric acid. In the same way

Strontium gives a crimson-red, and

Calcium gives a yellowish-red flame.

Magnesium, when ignited, then moistened with cobalt nitrate solution and again ignited, is colored a faint flesh-pink.

II. The Common Heavy Metals Including the Alloys and Amalgams.

1. Easily Volatile; Form a Coating or Disappear.

Mercury is completely volatilized, leaving at most a distant, gray coating. On plaster this is very distinct. Some salts of mercury form white coatings. If mixed with dry sodium carbonate and heated in a matrass, globules of mercury are deposited in the cool part of the tube. On plaster with sulphur and potassium iodid it gives a scarlet coating, with yellow; if quickly heated this is dull and black.

Arsenic volatilizes completely with distinct white incrustation. It gives, when vaporized, a garlic odor. In a matrass with sodium carbonate, most compounds give a dark ring with a metallic luster. This is metallic arsenic. No globules can be perceived.

Antimony gives brittle, white metallic globules. These produce white fumes when heated in the oxidizing flame and a distinct white incrustation with a bluish border. The metal continues to burn after removing the flame, finally surrounding itself with crystals of the oxid. If dropped on the floor when melted it rolls and leaves a white track behind. It imparts a greenish-blue color to the oxidizing flame. Heated on plaster with sulphur and potassium iodid it gives an orange coating stippled with peach red.

Bismuth gives reddish-white, brittle metallic globules with a yellow coating. When mixed with sulphur and potassium iodid and heated with a small, oxidizing flame a brilliant scarlet coating is produced, with a yellow one at a greater distance; with the last reagents on plaster, a chocolate-brown coating with underlying scarlet; with ammonia this becomes orange-yellow and cherry-red.

Lead forms white, malleable metallic globules with a

yellow coating which has a white edge. The flame is a bluish-white. Heated with sulphur and potassium iodid the volatile coating is a bright yellow.

Cadmium has a reddish-brown incrustation near the assay with a yellow one farther away. No globules can be observed. In a matrass the metal volatilizes condensing to bright globules on cooling.

2. The Non-volatile Metals or those which Vaporize with Difficulty, and which Color the Borax Bead.

Many of these impart a definite color to a bead of fused borax, held in a loop of platinum wire. To as far as possible avoid the presence of fusible metals which would alloy the platinum the test substance may be roasted on charcoal to vaporize the volatile ones and to oxidize most of the others, with any sulphur that may be present. This is accomplished by heating a thin layer with a gentle oxidizing flame so as not to fuse it, turning the particles in order to thoroughly oxidize or volatilize them. Some of the metals which may remain cannot be oxidized at all, and in some cases the oxidation is incomplete.

At the end of a platinum wire make a loop about an eighth of an inch in diameter by winding it around a match or the point of a pencil. Heat it and after dipping it into powdered borax heat the mass until it fuses to a clear, colorless bead. If this is colored the wire was not clean and the bead should be removed by straightening the wire and a new one made. Touch the hot bead to a minute fragment of the oxidized residue which will adhere, then heat again, first in the oxidizing flame, then in the reducing flame of the blow-pipe. Notice the color which is given to the bead. The latter should, with most metals, remain transparent. If it becomes black it is because too much of the substance has been added.

Manganese in the oxidizing flame gives a reddish-purple which becomes colorless in the reducing flame. A small portion fused into a bead of potassium nitrate and sodium carbonate becomes deep green.

Chromium gives an emerald-green bead, there being little change produced by the different flames. In the bead of potassium nitrate and sodium carbonate, a yellow color is produced. If this mass is dissolved in a drop of water it makes a bright yellow solution.

Cobalt produces a deep blue bead, the color being unchanged in the reducing flame. Heated alone on charcoal in the reducing flame the metal is obtained, a black magnetic powder.

Iron colors the bead yellow to reddish in the oxidizing flame, the shade being darker when hot, and also as the amount of iron is increased. In the reducing flame it is colorless to bottle green. Heated alone on charcoal, iron and its compounds give a black powder which is attracted by a magnet.

Nickel when oxidized gives a bead, violet when hot and brown when cold. On the charcoal the reducing flame converts its compounds to metallic nickel, a black, magnetic powder. This shows a metallic luster on rubbing in a mortar.

Copper colors the borax green as it is taken from the oxidizing flame, changing to a blue as it cools. In the reducing flame the bead is colorless unless a large amount of the metal is present, when it becomes a brownish-red and opaque on cooling. On charcoal compounds of copper are reduced to the metal which fuses to a malleable globule. In the reducing flame the color of the metal is seen, but on removing it from the flame, or on heating in the oxidizing flame, it is covered with a black oxid. Copper gives a green color to the flame; the chlorid which

may be formed by moistening with hydrochloric acid gives a blue one.

3. Metals which Volatilize with Difficulty or not at all and do not Color the Borax Bead.

After heating in order to as far as possible remove the volatile metals, if such are present, place the residue on a clean piece of charcoal and heat again with the oxidizing and then the reducing flame.

Zinc gives, near the substance, a coating which is yellow when hot and white after it has cooled. Moisten this with cobalt nitrate solution and heat again to as high a temperature as can be produced. The coating is changed to a bright green.

Tin has a coating, on or very near the assay but no metallic globules. It is yellow when hot and white when cold. Moistened with cobalt nitrate and ignited it becomes bluish-green. On plaster with sulphur and potassium iodid it gives a brownish-orange coating.

Aluminum gives a non-volatile incrustation on the substance heated, which is white both hot and cold. Ignition after moistening with cobalt nitrate produces a bright blue color.

Silver gives white, malleable metallic globules. A dark red coating is formed near the assay but only after very long heating.

Gold fuses to yellow metallic globules without a coating. It is soluble in aqua regia but not in nitric acid.

Platinum remains infusible on the charcoal and gives no coating. If reduced from its compounds it is a fine, black powder. If it is in larger masses it is of a white color.

Practical Exercises.

By blow-pipe analysis determine the bases of unknown compounds furnished by the instructors, then the names of

unknown single metals, finally the composition of simple alloys.

To fix in mind some of the more important properties of the metals the following questions should in all cases be answered.

Ease of reduction? degree of fusibility? of volatility? ease of oxidation? difference at high temperatures and the ordinary ones? If an oxid is formed what is its color? is this changed with the temperature? is the metal malleable or brittle? hard or soft?

Try to classify the metals on the basis of each of these properties into,

1. Very readily changed.
2. Changed without difficulty.
3. Changed with difficulty.
4. No change effected.

Questions for Further Study on Blow-Pipe Analysis.

For what reason is the charcoal under the test substances heated to a red heat in the blow-pipe analysis? What chemical action takes place when chlorates and nitrates are heated on charcoal? To what class of chemical agents do these compounds belong? Where are they used when this property is of value? Are there any substances with which they would be incompatible? When is a high heat necessary to produce this chemical reaction? What is an acid salt? What is the action of the acid potassium sulphate when heated with a nitrate? Why does cupric oxid in the presence of a chlorate give a blue flame instead of the ordinary green one? How does moisture cause decrepitation? Why is it necessary to heat sulphur to obtain an odor? What is the black compound formed on the silver coin when it is brought in contact with moist sodium sulphid? Why is the water

added before the discoloration can be produced? What brings about the change of a sulphate to a sulphid when treated in this manner? What becomes of the bases of a silicate when it is heated with microcosmic salt? What is the black substance produced when organic compounds are heated? What compounds are formed when graphite is deflagrated with potassium chlorate? When ammonium chlorid is volatilized on charcoal is it a complete chemical decomposition or a physical change? Is calcium oxid fusible? What application is made of this property and the fact that it is very luminous at high temperatures? Why does the addition of hydrochloric acid to some of these compounds make a brighter flame? How do the compounds of the alkaline earths compare with those of the alkali metals in strength of alkalinity? Are there any other of their compounds except the oxids which will have the same effect on litmus paper?

What is the action of sodium carbonate in setting mercury free from its salts? Which would be the better way to detect small quantities of mercury, by heating on charcoal or in a matrass? Is the sodium carbonate used for the same purpose with arsenic compounds? How would you explain the absence of metallic globules when cadmium, zinc, tin and aluminum compounds are heated on charcoal and their production when the same process is applied to compounds of lead or bismuth? Why is platinum wire used for supporting the borax bead in preference to wire of other metals? What causes the swelling of the powdered borax in making the transparent bead? How does the action of the borax in the bead explain its usefulness in the soldering of two pieces of metal? How can you explain the fact that some metals, like iron, give one color when the bead is heated in the oxidizing flame, and a different one in the reducing flame? What does the position of the coating on the charcoal show as regards the volatility of the metals?

THE REAGENTS MOST COMMONLY USED IN ANALYTICAL CHEMISTRY.

When not otherwise stated the strength given is the weight of the reagent contained in a hundred parts of the solution and distilled water is the solvent.

Name.	Formula.	Percentage Strength.	Method of Preparation.	Should give Negative Results when Treated as Follows:
Acetic acid.	CH_3CO_2H	6		$BaCl_2$ (178); $AgNO_3 + HNO_3$, (239); no residue upon evaporation of 10 cc.
Ammonium carbonate.	$(NH_4)_2CO_3$	10		$BaCl_2$ after acidifying with HCl (178); $AgNO_3$ after acidifying with HNO_3 (239); no residue upon igniting.
Ammonium chlorid.	NH_4Cl	10		$BaCl_2$ after acidifying with HCl (178); no residue upon ignition; no dark residue when evaporated to dryness.
Ammonium hydrate.	NH_4OH	5	Dilute the stronger ammonia[1] with water.	$BaCl_2$ after acidifying with HCl (178); equal volume of water and $Ca(OH)_2$ (185); $(NH_4)_2S$ (Table II); no residue after evaporation; $AgNO_3$ after acidifying with HNO_3 (239).
Ammonium molybdate.	$(NH_4)_2MoO_4 \cdot 4H_2O$	5	Dissolve the salt in four parts of dilute ammonium hydrate, then slowly pour into 15 parts of 30% HNO_3.	No yellow precipitate after several days' standing.

[1] "Stronger ammonia" is not 100%.

Name.	Formula.	Percentage Strength.	Method of Preparation.	Should give Negative Results when Treated as Follows:
Ammonium oxalate.	$(NH_4)_2C_2O_4$, H_2O	5		Same as carbonate.
Ammonium sulphid.	$(NH_4)_2S$		Pass H_2S gas into three parts of ammonium hydrate as long as it is absorbed. Then add two parts of ammonium hydrate.	No residue on evaporation; no precipitation with $MgSO_4$ (11).
Yellow ammonium sulphid.	$(NH_4)_2S_x$		Add flowers of sulphur to the last, and allow to dissolve.	No colored residue on evaporation.
Aqua regia.		As desired.	3 parts of HCl, 1 part of HNO_3; should be freshly prepared.	
Barium carbonate.	$BaCO_3$		Is insoluble in water. To be shaken with water and used before settling.	No insoluble residue with dilute HCl; with this solution no precipitate by H_2S (Table IV) or NH_4OH and $(NH_4)_2S$ (Table II); dissolved in acetic acid no decolorization of a drop of indigo after warming with H_2SO_4 (253); HNO_3 + $AgNO_3$ (239).
Barium chlorid.	BaCl, $2H_2O$	5		As $BaCO_3$, except last test.
Bromin water.	Br		Add enough to water so that after shaking a few drops of Br remain in bottom.	No residue on evaporation over steam-bath.

Name.	Formula.	Percentage Strength.	Method of Preparation.	Should give Negative Results when Treated as Follows:
Calcium hydrate.	$Ca(OH)_2$		Saturate water with the pure hydrate, and, after settling, decant or filter off the clear liquid. Must be kept away from air.	Should not remain clear when breathed into (185).
Cochineal.			In 100 parts of 20% alcohol macerate 1 part of powdered cochineal and, after settling, decant the clear liquid for use.	
Congo-red.		1	Dissolve in water.	
Copper sulphate.	$CuSO_4, 5H_2O$	5		
Erdmann's reagent.			Add six drops of 40% nitric acid to 100 cc. of water and to 10 drops of this solution add 20 grm. concentrated sulphuric acid.	
Fröhde's reagent.			Dissolve 0.1 grm. of sodium molybdate in 10 cc. of concentrated sulphuric acid. It must be freshly prepared as it is unstable.	
Ferric chlorid.	$FeCl_3$	5		$K_3Fe(CN)_6$ (63); no strong odor of HCl from the solid; no color in the filtrate after precipitation by NH_4OH and no residue when this is evaporated.
Ferrous sulphate.	$FeSO_4, 7H_2O$	5	Dissolve in recently boiled water and preserve away from the air.	No red color with KSCN (64), no insoluble residue; but little change upon blue litmus paper; HCl and H_2S. (Table IV.)

Name.	Formula.	Percentage Strength.	Method of Preparation.	Should give Negative Results when Treated as Follows:
Hydrochloric acid (concentrated), sp. gr. 1.20.	HCl	40		10 parts water and a few drops of $BaCl_2$ (178); only very slight residue after evaporation; equal volumes of water and H_2S after an hour (Table IV); no color in solution.
Hydrochloric acid, dilute.	HCl	5	One volume of the strong acid diluted with nine volumes of water.	As with the concentrated acid.
Hydrogen sulphid.	H_2S		Generate the gas by the action of HCl or H_2SO_4 on ferrous sulphid. To make the solution, pass the gas into water as long as it dissolves. Keep away from air.	
Indigo.	$C_{20}H_{10}N_2O_2$		Dissolve enough indigo carmine to give the color desired.	
Lacmoid.		0.2	Dissolve in dilute alcohol. Should be kept in the dark.	
Lead acetate.	$Pb(C_2H_3O_2)_2.3H_2O$	5		With ammonium hydrate no yellow color (61) or blue filtrate (78); $HNO_3 + AgNO_3$ (239); does not decolorize indigo when warmed with H_2SO_4 (248).

Name.	Formula.	Percentage Strength.	Method of Preparation.	Should give Negative Results when Treated as Follows:
Litmus solution.			Extract the powder with hot alcohol; discard this and extract with water, allow to settle and decant. Neutralize (purple color) with NaOH and H_2SO_4. Air must be allowed to enter the bottle in which it is preserved.	
Litmus paper.			Color the above solution red or blue by a drop of H_2SO_4 or NaOH and saturate absorbent paper.	
Magnesium sulphate.	$MgSO_4, 7H_2O$	5		NH_4Cl+NH_4OH (203); H_2S (Table IV); HNO_3+AgNO_3 (239).
Mercuric chlorid.	$HgCl_2$	5		No residue on ignition; no insoluble residue in water.
Metaphenylendiamin.	$C_6H_4(NH_2)_2$	0.5	Dissolve in water and acidify slightly with H_2SO_4.	The solution should be colorless.
Methyl orange.	$C_{14}H_{15}N_3O_3S$	0.1		No precipitate with alkalies, or $BaCl_2$ or brownish-yellow with HCl from con. solution; no violet or green with $AuCl_3$.
Methyl violet.		1	Dissolve in water.	
Nessler's reagent.			13 grm. $HgCl_2$ in 800 cc. of water, then 35 grm. KI, when the precipitate should be dissolved. Add $HgCl_2$ until a permanent turbidity forms, then 160 grm. KOH. Dilute to a liter; let it settle and use clear liquid.	

Name.	Formula.	Percentage Strength.	Method of Preparation.	Should give Negative Results when Treated as Follows:
Nitric acid (concentrated), sp. gr. 1.42.	HNO_3	65–70		No residue on evaporation; after considerable dilution with water no reaction with $BaCl_2$ (178); water + $AgNO_3$ (239); ammonium hydrate till alkaline, then $(NH_4)_2S$ (Table IV); and $(NH_4)_2C_2O_4$ (14).
Nitric acid, dilute.	HNO_3	10	Dilute one volume of the strong acid with six of water.	Same as for the concentrated acid.
Platinic chlorid.	$PtCl_4$	1		Leaves no insoluble residue in alcohol.
Phenolphthalein.	$C_{20}H_{14}O_4$	1	Dissolve in 50 % alcohol.	No residue when dissolved in alcohol.
Potassium chromate.	K_2CrO_4.	1		$HCl+BaCl_2$ (178); the solid warmed with equal parts of water and strong H_2SO_4 gives no red fumes (Cl).
Potassium dichromate or bichromate.	$K_2Cr_2O_7$	5		As the chromate.
Potassium cyanid.	KCN	5		No dark color in solid or in the precipitate with lead acetate (154) no insoluble residue in hot dilute alcohol.
Potassium ferricyanid.	$K_3Fe(CN)_6$	5		No blue with $FeCl_3$ (62).
Potassium ferrocyanid.	$K_4Fe(CN)_6$, $3H_2O$	5		$HCl+BaCl_2$ (178).
Potassium iodid.	KI	5		No blue color with litmus; H_2S (Table IV); $BaCl_2$ (178); $FeCl_3+FeSO_4+NaOH+HCl$ (247); no blue color with starch solution and dilute H_2SO_4.

Name.	Formula.	Percentage Strength	Method of Preparation.	Should give Negative Results when Treated as Follows:
Potassium hydrate.	KOH	5		5 grm. gives clear solution with 20 cc. water; this when acidified with HCl and made alkaline with NH_4OH forms no precipitate on long standing (31); the filtrate or solution from the last gives no precipitate with $(NH_4)_2S$ (Table II) or $(NH_4)_2C_2O_4$ (14); no residue in 90% alcohol; no results from $HCl+BaCl_2$ (178); HNO_3+AgNO_3 (239); H_2SO_4+ indigo + heat (253).
Potassium permanganate	$KMnO_4$	0.1		0.5 grm. boiled with 2 cc. alcohol and 25 cc. of water, then HNO_3 added precipitates with neither $Ba(NO_3)_2$ (178) nor $AgNO_3$ (239); when decolorized by oxalic acid con. $H_2SO_4+FeSO_4$ give no color (251).
Potassium sulphocyanate.	KSCN	5		$(NH_4)_2S$ (Table II); $BaCl_2$ (178).
Rosolic acid.	$C_{20}H_{16}O_3$	1	Dissolve in 60% alcohol.	
Silver nitrate.	$AgNO_3$	5		0.5 grm. with 0.5 cc. water and 20 cc. absolute alcohol leaves no insoluble residue (KNO_3 or AgCl).

Name.	Formula.	Percentage Strength.	Method of Preparation.	Should give Negative Results when Treated as Follows:
Sodium carbonate.	Na_2CO_3, $10H_2O$	10		After acidifying with HCl and evaporating to dryness no residue insoluble in water (SiO_2); with $HCl + BaCl_2$ (178); with $HNO_3 + AgNO_3$ (239); with $(NH_4)_2S$ or H_2S after acidifying.
Sodium hydrate.	NaOH	5		Same as potassium hydrate.
Sodium phosphate.	Na_2HPO_4, $12H_2O$.	5		With HCl no effervescence and with $BaCl_2$ no precipitate (178); HNO_3+ $AgNO_3$ (239); with strong H_2SO_4 does not decolorize indigo (253); H_2S (Table IV); $(NH_4)_2S$ (Table II).
Starch solution.	$(C_6H_{10}O_5)_x$	1	Mix with cold water, then heat to boiling. Decomposes on standing.	
Sulphanilic acid.	$C_6H_4NH_2SO_3H$		See tests for nitrites.	
Sulphuric acid (concentrated), sp. gr. 1.84.	H_2SO_4	100		No dark color; no residue on evaporation; does not decolorize indigo (253); no precipitate on dilution with water or alcohol (159); no precipitate after neutralization with NH_4OH by $(NH_4)_2S$ (Table II) or $(NH_4)_2C_2O_4$ (14); 10 volumes of water and $AgNO_3$ (239); Gutzeit's test (118).

Name.	Formula.	Percentage Strength.	Method of Preparation	Should give Negative Results when Treated as Follows:
Sulphuric acid, dilute.	H_2SO_4	10	One volume is slowly poured into 17 volumes of water.	Same as with strong acid.
Tin chlorid for Bettendorf's test.	$SnCl_2$		One part of the crystallized salt in two parts of HCl, sp. gr. 1.19.	No color or precipitate on boiling (120); water and $BaCl_2$ (178).
Tin chlorid for Hg test.			Dissolve the metal in hot strong HCl and dilute with water. Must have some undissolved metal in the liquid to be permanent.	Same as above.
Turmeric paper.			After washing the powdered turmeric root in water and drying, extract it with alcohol and with this solution saturate white paper.	
Vanadium sulphate.		0.5	Dissolve one part of ammonium vanadate in concentrated sulphuric acid.	

THE CHEMICAL ELEMENTS

with their Symbols and Atomic Weights.

THESE are from the report of the International Committee on Atomic Weights, 1904. Both those based upon the atomic weight of hydrogen as the unit, and those from O = 16 are given.

NAME	SYMBOL.	AT. WT. (H = 1.000)	AT. WT. (O = 16.00)	NAME.	SYMBOL.	AT. WT. (H = 1.000)	AT. WT. (O = 16.00)
Aluminum	Al	26.9	27.1	Neon	Ne	19.9	20
Antimony	Sb	119.3	120.2	Nickel	Ni	58.3	58.7
Argon	A	39.6	39.9	Niobium [2]	Nb	93.3	94
Arsenic	As	74.4	75.0	Nitrogen	N	13.93	14.04
Barium	Ba	136.4	137.4	Osmium	Os	189.6	191
Beryllium [1]	Be	9.03	9.1	Oxygen	O	15.88	16.00
Bismuth	Bi	206.9	208.5	Palladium	Pd	105.7	106.5
Boron	B	10.9	11	Phosphorus	P	30.77	31.0
Bromin	Br	79.36	79.96	Platinum	Pt	193.3	194.8
Cadmium	Cd	111.6	112.4	Potassium	K	38.86	39.15
Cæsium	Cs	131.9	132.9	Praseo-dymium	Pr	139.4	140.5
Calcium	Ca	39.8	40.1	Radium	Ra	223.3	225
Carbon	C	11.91	12.0	Rhodium	Rh	102.2	103.0
Cerium	Ce	139.2	140.25	Rubidium	Rb	84.8	85.4
Chlorin	Cl	35.18	35.45	Ruthenium	Ru	100.9	101.7
Chromium	Cr	51.7	52.1	Samarium	Sa	148.9	150.0
Cobalt	Co	58.56	59.0	Scandium	Sc	43.8	44.1
Copper	Cu	63.1	63.6	Selenium	Se	78.6	79.2
Erbium	Er	164.8	166	Silicon	Si	28.2	28.4
Fluorin	F	18.9	19	Silver	Ag	107.12	107.93
Gadolinium	Gd	155	156.2	Sodium	Na	22.88	23.05
Gallium	Ga	69.5	70	Strontium	Sr	86.94	87.6
Germanium	Ge	71.9	72.5	Sulphur	S	31.83	32.06
Gold	Au	195.7	197.2	Tantalum	Ta	181.6	183
Helium	He	4	4	Tellurium	Te	126.6	127.6
Hydrogen	H	1.000	1.008	Thallium	Tl	202.6	204.1
Indium	In	113.1	114	Thorium	Th	230.8	232.5
Iodin	I	125.90	126.85	Thulium	Tu	169.7	171
Iridium	Ir	191.5	193	Tin	Sn	118.1	119.0
Iron	Fe	55.65	55.9	Titanium	Ti	47.7	48.1
Krypton	Kr	81.2	81.8	Tungsten	W	182.6	184.0
Lanthanum	La	137.9	138.9	Uranium	U	236.7	238.5
Lead	Pb	205.35	206.9	Vanadium	V	50.8	51.2
Lithium	Li	6.98	7.03	Xenon	X	127	128
Magnesium	Mg	24.18	24.36	Ytterbium	Yb	171.7	173
Manganese	Mn	54.6	55.0	Yttrium	Y	88.3	89.0
Mercury	Hg	198.8	200.0	Zinc	Zn	64.9	65.4
Molybdenum	Mo	95.3	96.0	Zirconium	Zr	89.9	90.6
Neodymium	Nd	142.5	143.6				

[1] Also called glucinum.

[2] Also called columbium.

THE METRIC SYSTEM.

In all work in chemistry the metric system of weights and measures is used instead of the older ones formerly in vogue. It is based upon the meter (39.37 inches) which is the unit of length. The hundredth part of this is the centimeter and a cube of water at 4° C., each side of which is a centimeter, weighs a gramme — the unit of weight. One-tenth the length of the meter is a decimeter and a cube which has a side of this dimension contains a liter — the unit of capacity. The fractions and multiples of these are the following:

Measures of Length.

10 millimeters (mm.)	=	1 centimeter (cm.).
10 centimeters	=	1 decimeter.
10 decimeters	=	1 meter (m.).
10 meters	=	1 decameter.
10 decameters	=	1 hectometer.
10 hectometers	=	1 kilometer.

Measures of Weight.

10 milligrammes (mg.)	=	1 centigramme.
10 centigrammes	=	1 decigramme.
10 decigrammes	=	1 gramme (g. or gm.).
10 grammes[1]	=	1 decagramme.
10 decagrammes	=	1 hectogramme.
10 hectogrammes	=	1 kilogramme (kilo.).

[1] The *me* is often dropped in the names of these denominations. It is perhaps preferable that it should be retained to avoid any danger of reading grain for gram.

Measures of Volume.

10 milliliters	=	1 centiliter.
10 centiliters	=	1 deciliter.
10 deciliters	=	1 liter (l.).
10 liters	=	1 decaliter.
10 decaliters	=	1 hectoliter.
10 hectoliters	=	1 kiloliter.

In volumetric analysis it is important to remember that one cubic centimeter of water weighs one gramme, and that a liter contains 1,000 cubic centimeters. A liter of water therefore weighs 1,000 grammes or one kilogramme (kilo.).

For conversion into other systems we have:

1 meter	=	39.37 inches.
1 foot	=	0.304 meter.
1 liter	=	61.03 cu. in. = 1.06 U. S. qts.
1 liter	=	33.81 U. S. fluidounces.
1 gramme	=	15.43 grains.
1 grain	=	0.0648 gramme.
1 ounce (apoth.)	=	31.1 grammes.
1 ounce (avoirdupois)	=	28.35 grammes.
1 pound (apoth.)	=	373.2 grammes.
1 pound (avoirdupois)	=	453.6 grammes.

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